"Synthesis of Aromatic Dibenzyl Disulfide using H_2S and Solid Reusable Resin as Catalyst"

Thesis Submitted by

DOROTHY CHETIA (212CH1496)

In partial fulfillment for the award of the Degree of

MASTER OF TECHNOLOGY

IN

CHEMICAL ENGINEERING

Under the guidance of

Dr. SUJIT SEN

DEPARTMENT OF CHEMICAL ENGINEERING

NATIONAL INSTITUTE OF TECHNOLOGY

ROURKELA-769008

May, 2014

राष्ट्रीय प्रौद्योगिकी संस्थान राउरकेला

Natioanl Institute of Technology Rourkela

CERTIFICATE

This is to certify that the thesis entitled **"Synthesis of Aromatic Dibenzyl Disulfide using H_2S and Solid Reusable Resin as Catalyst",** submitted by **Dorothy Chetia (212CH1496)** to National Institute of Technology Rourkela, in fulfillment of the requirements of the degree of Master of Technology in Chemical Engineering is a bonafide record of the research work carried out by her, in the Department of Chemical Engineering, National Institute of Technology, Rourkela under my supervision and guidance. Miss Dorothy has worked on this topic from July, 2013 until May, 2014 and the thesis, in my opinion, is worthy of consideration for the award of the degree of "Master of Technology" in accordance with the regulations of this Institute. The results embodied in the thesis have not been submitted to any other University or Institute for the award of any degree or diploma.

Date: 23 May 2014

Dr. Sujit Sen

Department of Chemical Engineering

National Institute of Technology

Rourkela, Orissa-769008

ACKNOWLEDGEMENT

I wish to express my heartily gratitude to my guide Dr. Sujit Sen for his valuable guidance with constant flow of existing new ideas and contagious enthusiasm through my work. My association with my guide will remain a memorable part of my life. I want to thank sir for constantly motivating me through him valuable counsel as well as excellent tips to build my research and writing skills.

I want to acknowledge the support and encouragement given by Priya Nakade, Ujjal Mondal and Gaurav Singh throughout the period of my work.

I also take this opportunity to express my sincere thanks to Dr. R. K. Singh, Head of Department of Chemical Engineering for making available necessary facilities to complete this research work. I am also grateful Dr. B. Munshi and all other faculty members of department for their help whenever sought for.

I am obliged to all my friends for their friendships and encouragements. Finally, the thesis would not have been completed without the support of the most important people in my life − my family. I sincerely wish to thank my parents, for their unconditional love and constant encouragement.

Date- 23/05/2014

DOROTHY CHETIA
(212CH1496)

LIST OF FIGURES

LIST OF TABLE

LIST OF ABBREVIATIONS

PTC	Phase Transfer Catalysis
BC	Benzyl Chloride
BM	Benzyl Mercaptan
DBS	Dibenzyl Sulfide
DBDS	Dibenzyl Disulfide
DEA	Diethanolamine
DIPA	Diisopropanoloamine
GLC	Gas Liquid Chromatography
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
OVAT	One variable at a time
ppm	Parts per million
TEA	Triethanolamine TPC Tri Phase Catalyst

ABSTRACT

During hydro desulfurization or hydro treatment of crude oil in petroleum refineries, one or more gaseous by products are produced with hydrogen sulfide (H_2S) infused into it. Since the presence of H_2S, corrodes the process equipment and is highly toxic to the environment, it is eliminated from the gas stream and transformed into harmless forms. In general, H_2S from gas stream is removed using amine treating unit and is treated in the Claus unit for the production of elemental sulfur. This elemental sulfur is used mostly to produce sulphuric acid and also in rubber industries. But in Claus process valuable hydrogen energy is lost and requires exact process control over ratio of oxygen to hydrogen sulfide feed. Therefore, an alternative process which could transform H_2S to valuable chemicals, is greatly welcome in the process industry in improving the sulfur disposal problem. H_2S laden gas can be used in a more beneficial way by absorbing into aqueous alkanolamine like monoethanolamine (MEA) and then use this reagent to produce fine chemicals like disulfides, thioether, mercaptans, , amines etc., which have high usability and good market value. These organo-sulfide such as Dibenzyl disulfide (DBDS) find their application in manufacturing corrosion inhibitors, fragrance compounds, high pressure lubricant additives and other organic compounds. Since the alkanolamine phase and the organic phase are not miscible, to carry out this biphasic reaction, phase-transfer-catalyst (PTC) has been tired out a few times and often the application of PTC gives enhancement in reaction rate, more conversion for reactants and better selectivity of desired products.

This work was carried out to study the synthesis of fine chemicals like Dibenzyl Disulfide (DBDS) and using H_2S-rich monoethanolamine (MEA) and benzyl chloride (BC) under Liquid-Liquid-Solid phase transfer catalysis with a tri-phase catalyst. Owing to its solid state, availability, cost and reusability, Amberlite IR 400 is selected as a PTC. A parametric study was carried out which emphasized upon the impact of catalyst loading as one of the process variables on the conversion of benzyl chloride and selectivity of DBDS and parametric study with these substances revealed 100 % selectivity for desired product at ambient condition. The effects are utilized to establish a suitable mechanism of the reaction to explain the course of the reaction. The overall objective of this study is to maximize conversion of reactant BC and selectivity of DBDS.

Keywords: Hydrogen Sulfide; Alkanolamines; Dibenzyl Disulfide; Liquid-Liquid-Solid Phase Transfer Catalysis; Mechanism; Selectivity; Conversion.

CONTENTS

Chapter 1

INTRODUCTION

Chapter 1
INTRODUCTION

1.1 SOURCE OF HYDROGEN SULFIDE:

About 90 % of the hydrogen sulfide gas available in the air originates from the natural resources like volcanoes, hot springs and underwater thermal vents. Hydrogen sulfide is released into the air as a result of the breakdown of dead plant and animals, particularly when this happens in damp conditions with inadequate supply of oxygen, for example in swamps and sewers**.** This process is known as anaerobic digestion. Maximum man made hydrogen sulfide is not produced from industry, merely as a by-product of manufacture. Anthropogenic discharges of H_2S into the air is the outcome of industrial processes, particularly from the extraction and purification of oil and mineral gas and from paper and pulp manufacturing, chemical manufacturing, however the gas is also present in sewage treatment plants, tanneries, waste disposal and coke oven plants. The principal source of anthropogenic hydrogen sulfide is as a by-product in the hydro-treatment process of natural gas and refined form of crude petroleum. H_2S can be liberated into air from anywhere where elemental sulfur occurs in contact with organic material, mainly at high temperatures. Atmospheric releases of hydrogen sulfide most significantly affect the public health because of the geothermal energy industry. The importance of hydro-treatment is increasing day by day in the refineries. This is imputable to the reason that the source of crude oil which are easy and light to process is progressively turning down besides the people working in the refineries all over the globe are enforced to hold down the sulfur and nitrogen concentration to that particular level set by the environmental protection agency. In the course of processes like hydro treatment and hydro-desulphurization of crude oil in coal and petroleum industries, one or more gaseous by products are produced with H_2S and NH_3 infused into it. The coal gas contains 3.3% H_2S and about 1.1% NH_3 as the primary non-hydrocarbon impurities. The variance in the composition of crude natural gas can be seen broadly from field to field. The content of H_2S ranges between 0.1 ppm and 150,000 ppm.

1.2 REASONS FOR REMOVAL OF H_2S:

Because of the environmental protection agency's rules and ordinance, the refineries all over the world are facing problems with the disposal of hazardous materials such as H_2S a satisfactory manner. The various lawsuits for the removal of H_2S gas are described as follows: (Occupational and safety health administration)

- Hydrogen sulfide is a highly noxious and volatile in nature. It may move along the ground and can also deposit in low lying, enclosed and poorly ventilated areas. With continuous low level exposure or at high concentration, the victim remains unaware and loses its ability to smell even though it still exists. Low concentrations affect the eyes, nose, throat and respiratory system, whereas high concentration leads to shock, breathless, rapidly unconsciousness, coma and death. If the level of H_2S gas exceeds 100 ppm, it would immediately be risky to life and health. For safety purpose, the material safety data sheet (MSDS) of H_2S should be referred**.**
- Hydrogen sulfide is a poisonous in very low concentrations, highly corrosive gas in the presence of air and the monetary value of continuous care and replacement of pipelines, pipes and other equipment makes the prospect of managing natural gas with high levels of H_2S to be breakeven at best. Gas stream must be made completely free from H_2S before use and preferably before transportation**.** Consequently, the amount of H_2S is limited to less than $0.25gm/100ft^3$ of gas in the case of pipeline specification (Thomas, 1990).

- Since hydrogen sulfide gas is a flammable gas and thus mixtures of gas and air can occur explosion**.** This gas/air mixture may travel to ignition source and flash back**.** If the mixture travels to the ignition source and as a result it gets ignited than the gas from the mixture burns to produce toxic vapours and harmful gases, namely sulfur dioxide. The existence of H_2S in the refinery gas streams can hamper the posterior processes by equipment degradation**,** increase in the process pressure requirements, increase in the gas compressor capacity, deterioration or deactivation of catalyst, unwanted side reactions etc.

1.3 INDUSTRIAL PROCESS FOR REMOVAL AND RECOVERY OF H_2S:

Many industrial processes have been developed for the removal and the recovery of H_2S from the fluid stream. Due to the acidic (weak acid) nature of H_2S, it can be removed by using some alkaline solution. Strong alkaline solution such as sodium hydroxide forms irreversible chemical reaction products and as a result cannot be utilized for the elimination of hydrogen sulphide from the gas streams. It becomes more unfavourable when the gas contains both hydrogen sulphide and carbon dioxide and the CO_2 concentration is more than 4% (Robin 1999). So, weak alkaline solutions like ammonia and alkanolamines are used for the removal and retrieval of the H_2S.

1.3.1 Ammonia based processes:

This process is utilized normally for eliminating acidic gases from flue gases produced by refineries, petrochemical industrial, and other helps. Removal of H_2S using aqueous ammonia has become a well-established process and well-practiced by Hamblin, 1973 and Harvey and Makrides, 1980. As stated by this process, H_2S and NH_3 rich gas stream passes through a H_2S scrubber and NH_3 scrubber placed in series. NH_3 scrubber is provided with stripped water from the top where ammonia is absorbed from the gas. The following ammonical solution is utilized as absorbent in H_2S scrubber. The solution which comes out from this unit carries ammonium sulphide, which is decomposed to yield hydrogen sulphide and ammonical liquor in the decandifier. The process is depicted in the figure below. The reactions are:

$$NH_3 + H_2O \rightarrow NH_4OH$$
$$NH_3 + H_2O \rightarrow NH_4HS$$
$$2NH_3 + H_2O \rightarrow [NH_4]_2S$$

The main advantages of using ammonia based process are:

- Ammonia based process is well acceptable for gas streams having both H_2S as well as NH_3. The elimination of ammonia and hydrogen is done in single step in ammonia process while in alkanolamine it is done in two steps.

- Ammonia is one of the most largely produced chemicals in the world for the reason that it is a low-cost solvent, does not degrade in the presence of O_2 and other species in the flue gas, and also less corrosive, in comparison to other amines. The effects of ammonia on environment and health are well considered and found more benevolent than amines. Ammonia has high CO_2 removal efficiency and low regeneration energy.
- When a gas carrying both CO_2 and H_2S comes in contact with aqueous ammonia solution, the H_2S is absorbed at a high rate. The selective absorption of H_2S and $CO_2$is feasible in liquid ammonia by changing the concentration of liquid ammonia. The selective absorption of H_2S can be done by using spray column and giving short time contact.

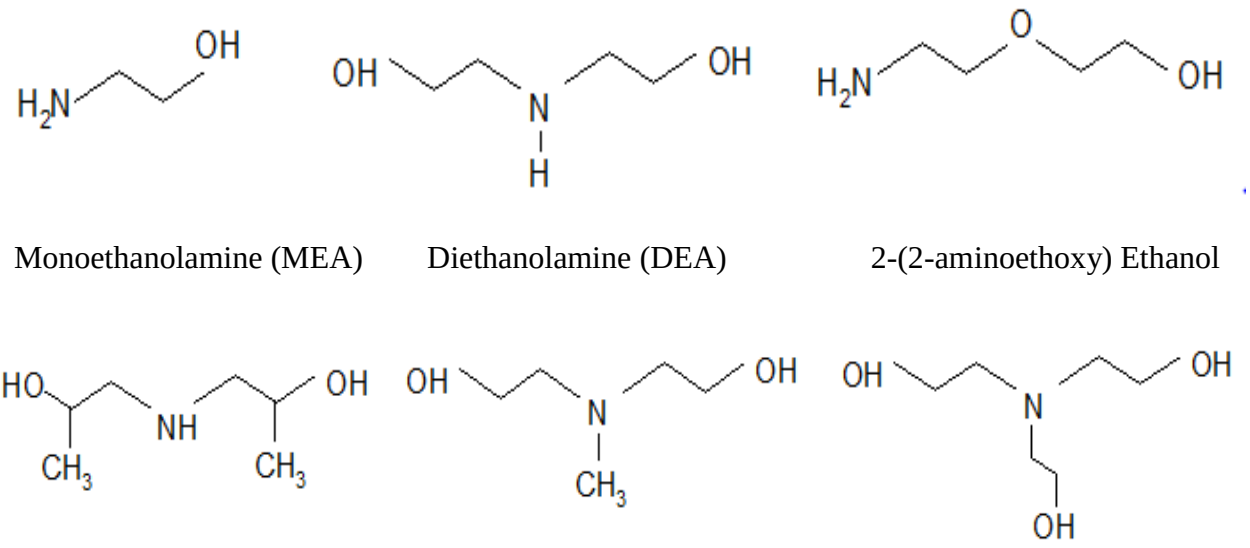
In spite of these advantages, the use of ammonical scrubbing has not been accepted all over the world in the gas treating technique as the ideal method for removing H_2S from a gas stream. This is for the reason of a number of functioning problems related with its applications (Hamblin, 1973), such as:

- High partial pressure of ammonia forces the scrubbing step to lead with relatively dilute NH_3 solutions or at relatively high pressures or a distinct water wash step after the NH_3 scrubbing step in order to eliminate NH_3 from the treated gas stream. Moreover, the utilization of dilute scrubbing solutions normally increases considerably the regeneration costs where the regeneration step is conducted at a significantly higher temperature than the scrubbing step.
- The regeneration of rich absorbent solution withdrawn from the scrubbing step consists of the use of soluble catalysts, so sulphur products get contaminated in the bearing of the catalyst.

1.3.2 Alkanolamine process:

In the past few years, alkanolamine process for the elimination of acid gases has achieved full acceptance. This is due to its merits such as ease of retrieval and low vapour pressure. In case of operational temperature, pressure and concentration of alkanaloamine, the low vapour pressures gets the operation more flexible. In this process, alkanolamine is used at a high concentration with the carelessness of a corrosion inhibitor. Triethanolamine(TEA) was the first

alkanolamine employed in early gas treating plants (Bottoms, 1930). However, this amine has been displaced to a large extent by Diethanol-amine (DEA) and Monoethanol-amine (MEA) which possess the advantage of lower molecular weights and are capable of effecting more complete H_2S removal. The most important amines that are used for purification of gas are Diethanolamine (DEA), Monoethanolamine (MEA) and Methyl- diethanolamine (MDEA). These amines replaced the Triethanol-amine due to its low capacity, its low reactivity and its relatively poor stability. These various amine mixtures have got mixture of names with formulated amines and Methyldiethanolamine based amines. Traditionally, MDEA has been known mainly due to its ability of selective absorption of H2S from a gas and giving CO_2 in the gaseous state. The structures of amines are**:**



Monoethanolamine (MEA) Diethanolamine (DEA) 2-(2-aminoethoxy) Ethanol

Diisopropanolamine (DIPA) Methayldiethanolamine (MDEA) Triethanolamine (TEA)

Fig 1.1: Structural Formulas of Different Alkanolamines

Each of the above alkanolamine has one hydroxyl as well as one amino group. The hydroxyl group helps to decrease the vapor-pressure and increase the solubility in water. The amino group offers the required alkalinity in water so that the H_2S gets absorbed.

1.3.3 Types of amines: Their advantages and disadvantages

1. Monoethanolamine (MEA)

Table 1.1: Advantages and Disadvantages of MEA

Advantages	*Disadvantages*
• The molecular weight of MEA is low and so it has high solution capability at moderate concentrations. • MEA is a comparatively strong base having a fast reaction rate and yielding a low CO_2 concentration. • It is the most reactive in the reaction.	• It is not possible for MEA to absorb H_2S selectively from gas stream carrying both H_2S and CO_2. • It is corrosive in nature. • Heat of reaction with H_2S and CO_2 leads to high energy requirement for stripping.

2. Diethanolamine (DEA)

Table 1.2: Advantages and Disadvantages of DEA

Advantages	*Disadvantages*
• It is less corrosive than MEA. • Due to low vapour pressure of DEA, it is suitable for operation. • Secondary amine like DEA is considerably less reactive with COS and CS_2 as compared to primary amine. So it is a better option for gas stream carrying both COS and CS_2.	• The reclaiming of contaminated DEA solution may require vacuum distillation DEA undergoes numerous irreversible reactions with CO_2 producing corrosive ruin products, and therefore, it may not be the optimal option for handling gases carrying a high CO_2 content.

3. Methyldiethanolamine (MDEA)

Table 1.3: Advantages and Disadvantages of MDEA

Advantages	*Disadvantages*
• Selectively absorb H_2S from gas streams containing both H_2S and CO_2. • Energy saving because of lower desorption temperature and lower heat of reaction compared to MEA and DEA. • It is less corrosive than MEA and DEA. • Since it has low vapor pressure, MDEA can be utilized in concentration up to 60 weight% in aqueous solutions with less evaporation losses.	• The cost of MDEA, which is higher than the other amines, has prevented its use.

1.3.4 Process:

The absorption reaction proceeds in absorber and then stripping of absorbed gases takes place in stripping column. The concentrated H_2S gas is then subjected to sulfur recovery. The basic flow diagram of the amine-based acid gas removal process is depicted in figure 1.2. Treatment with alkanolamine involves the circulation of the gas stream upward through the absorber, counter-current to the flow of aqueous alkanolamine solution. This solution coming from the bottom end of the absorber is heated with the help of heat exchanger with lean solution from the bottom of the stripping column where the absorbed gases are stripped of from the alkanol amine solution. The regenerated alkanolamine is then recycled to the absorber. The concentrated hydrogen sulfide gas obtained from top of the stripping column is then subjected to S recovery or disposal.

Reaction with H_2S:

$$2RNH_2 + H_2S \leftrightarrow [RNH_3]_2S$$

$$RNH_2 + H_2S \leftrightarrow RNH_3SH$$

Reaction with CO_2

$$2RNH_2 + CO_2 + H_2O \leftrightarrow [RNH_3]_2CO_3$$

$$RNH_2 + CO_2 + H_2O \leftrightarrow RNH_3CO_3H$$

$$2RNH_2 + CO_2 \leftrightarrow RNH - CO - ONH_3R$$

The process diagram:

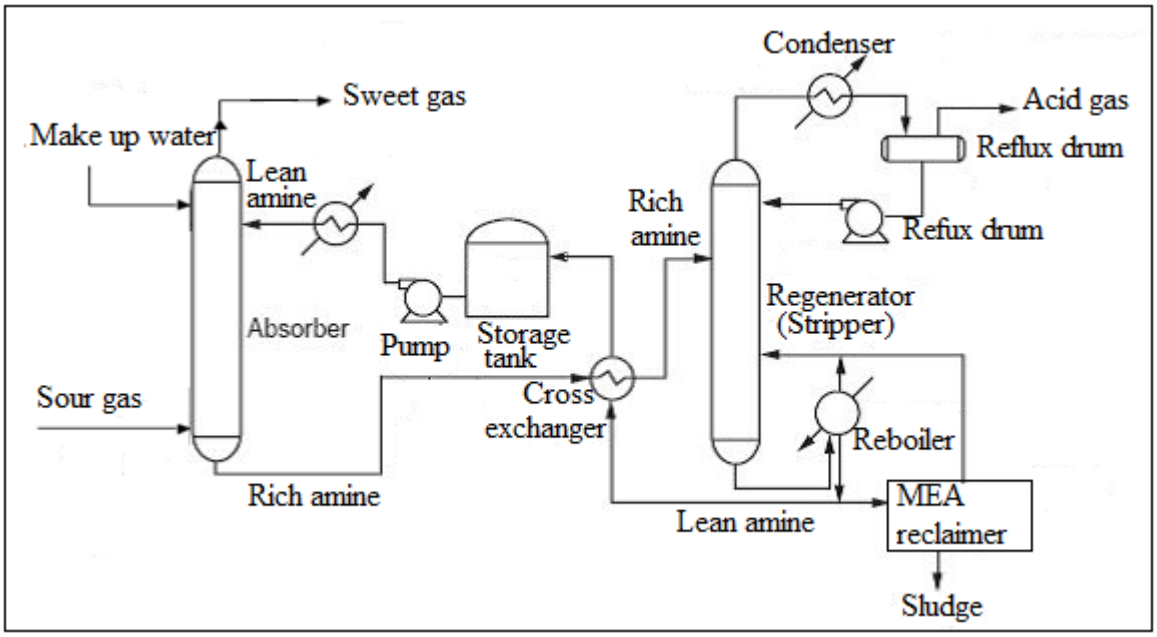


Fig 1.2: Flow Diagram of Amine Treating Process

1.4 CLAUS PROCESS OF SULFUR RECOVERY FROM H_2S GAS:

Through this process, the toxic H_2S gas is converted to non-toxic and useful elemental sulphur. It is a standard process used in industries. The basic purpose is to recover sulfur from the gaseous H_2S originated in natural gas as well as from the by-product gases. The by-product gases mostly originated from several gas treatment units found in various refineries, natural gas processing units, gasification plants etc. Hydrocarbons, sulfur dioxide or ammonia and hydrogen cyanide are present in these by-product gases. H_2S gas, i.e. separated by stream of gas using amine extraction, is provided to the Claus unit. In Claus unit, it is transformed in two steps i.e. the thermal step and the catalytic step. The H_2S rich gas in a reaction furnace reacts in a sub-stoichiometric combustion in the presence of air at temperatures between 1000 - 1400 ºC in the thermal step.

Claus gases with no more flammable substances apart from H_2S are burned in burner. This is a strongly exothermic oxidation reaction. The ratio of air to the acid gas is controlled in such a way that in total one third of all H_2S is converted to SO_2. This ensures a stoichiometric reaction in the catalytic step. In the catalytic step**,** the reaction gases leaving the sulfur condenser are reheated to 200 -350ºC and fed to the series of catalytic converter and sulfur condenser where H_2S react with SO_2 to produce elemental sulphur. The catalyst used in the catalytic converter is normally either activated aluminium (III) or titanium (IV) oxide. At last, a little quantity of H_2S remains in the tail gas known as the residual quantity. This residual is mixed with other trace of sulphur compounds to give overall sulfur recovery of about 99.8%. Sulfur is utilized for making sulfuric acid, greasepaints, fertilizers, medicine, manures, rubber products and elemental sulfur.

Reaction in the thermal step:

$$2H_2S + 2O_2 \rightarrow SO_2 + 2H_2O + S$$

Reaction in the catalytic step:

$$2H_2S + SO_2 \rightarrow 3S + 2H_2$$

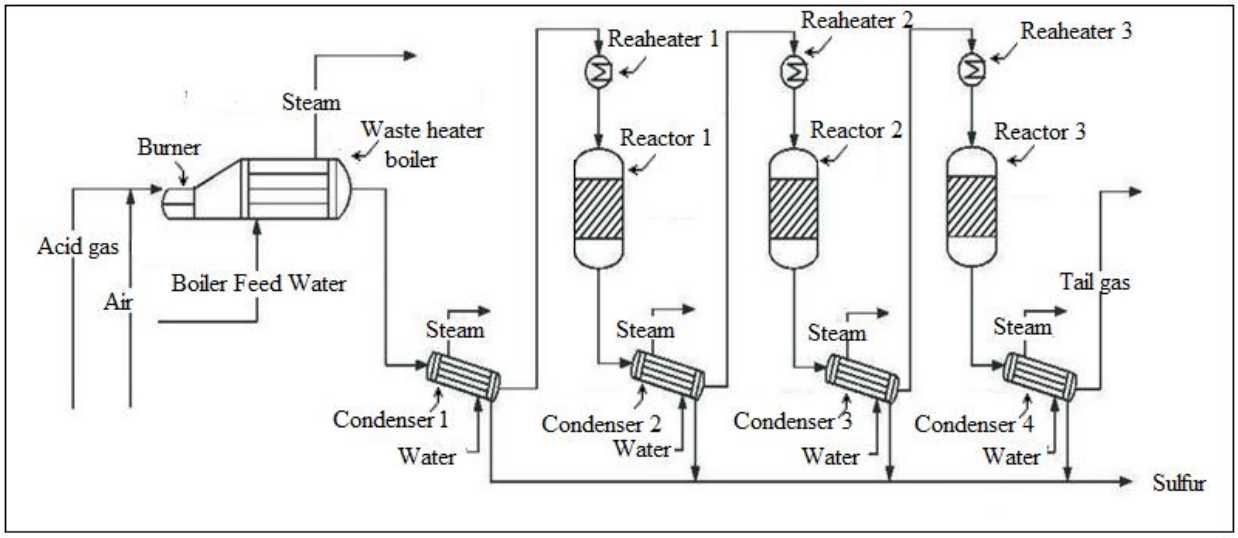


Fig. 1.3: Process Flow diagram of Sulfur Recovery Unit

However, the process has got certain disadvantages (Plummer et a.; 1994; Beazley et al.; 1986; Plummer and Zimmerman, 1986) such as:

- It operates at high temperatures.
- It needs exact process control over the ratio of oxygen to H_2S in the feed.
- The valuable hydrogen energy is lost in this process.
- It needs costly pre-treatment of the feed gas if CO_2 is present in high concentrations.
- The residue of Claus process i.e., the sulphur gas released to the atmosphere is usually too high to meet strict environmental guidelines. To obey these guidelines, it is crucial to add more Claus stages and/or employ a distinct tail gas clean-up process at great expense.

1.5 OTHER WAYS TO PROCESS SOUR GAS:

Amine extraction is not suitable for the treatment of H_2Sgases which contains high concentration of CO_2. Therefore such streams go through processing by CrystaSulf, a "liquid redox" process used for the treatment of natural gas.In such type of processes, a liquid solution carrying oxidized iron is used in substitution of air. As an emblem of novelty, H_2S Splitting Process is also being developed to make hydrogen as well as sulfur from H_2S.

1.5.1 CrystaSulf:

CrystaSulf is the name of a chemical process which has been developed specifically in refineries to separate H_2S from sour natural gas and gas streams (Deptt. of Energy Report)**.** CrystaSulf has reasonable operating costs and reasonable capital costs, which makes it a good fit for several mid-size sulfur retrieval applications. It is quite flexible process and can be used in two different cases i.e. direct removal of H_2S from gas stream or clause tail gas treatment. The liquid phase Claus reaction of H_2S with SO_2 is used to convert H_2S into sulfur and the sulfur thus obtained is then removed by filtration. In CrystaSulf process heavy liquid hydrocarbon gush out in a sudden and forceful stream through an absorber where the liquid comes in contact with H_2S rich gas streams. In the following step, H_2S gets absorbed from the gas stream and the resulting clean gas stream then leaves absorber. The H_2S existing the liquid reacts with the SO_2 to form elemental sulfur and water.

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$

1.5.2 Wet Oxidation LO-CAT Process:

A liquid phase oxidation process utilizes solution that are not noxious but a little alkaline which contains an iron chelate complex as a redox catalyst. This process involves the conversion of H_2S into elemental sulfur, taking into consideration the environmental issues**.** Gas stream carrying H_2S is contacted with aqueous LOCAT solution in a venture-scrubber. The H_2S absorbed in solution is instantly reacts with oxygen to form elemental sulfur**.** The reduced catalyst H_2S solution is regenerated by air in a vessel known as oxidizer. Sulfur is eliminated from the circulating solution by going down in the underside of the oxidizer or in a free-standing non-aerated vessel. Sulfur can be retrieved from the sulfur slurry by melting or via centrifuge. The process can take away to 99.9% of H_2S from gas flow with any H_2S concentration.

1.6 PRESENT WORK:

The current work was undertaken to develop low cost and environmentally benign alternatives to the Claus process for better consumption of H_2S present in several gas streams. The current work deals with various byproduct gases to be utilized for the synthesis of fine value added chemicals obtained from different chemical industries. In conformity with the present process, value-added chemicals were produced from the H_2S-rich aqueous ammonia or alkanolamine that could be obtained from scrubbing step of the corresponding ammonia- or alkanolamine-based process. In other word, the removal of H_2S was expected to be performed by conventional process. The current investigations are dedicated to:

.

- Synthesis of value-added fine chemicals like dibenzyl disulfide and dibenzyl sulfide using the H_2S -rich aqueous alkanolamines under three phase (liquid-liquid-solid) conditions in the presence of Amberlite IR 400 as PTC.
- Examine the influence of process variables like stirring speed, elemental sulfur loading, concentration of reactant, temperature, sulphide concentration, catalyst loading on the conversion of organic reactants as well as on the selectivity of products.
- Reusability of catalyst is also tested, which is the main advantage of using a solid catalyst over a liquid catalyst.

- Establishment of suitable mechanism utilizing the effects of several parameters on the rate of reaction as well as on the conversion to explain the course of the reaction.

1.7 PHASE TRANSFER CATALYSIS (PTC):

PTC is an exceptionally effective technology which improves environmental performance over pollution prevention, green chemistry and pollution treatment. There are reactions which are unable to take place since reactants are unapproachable to one another. The issue relating the carrying an organic water insoluble electrophilic reagent and water soluble nucleophilic reagent together has been arises. This issue was resolved conventionally by adding solvent that is both hydrophilic and lipophilic. An effective process developed over a last twenty five years is dissolving nucleophilic reagent into water and electrophilic reagent into organic solvent and then employed on a catalyst amount which transfer active anion from solid/aqueous phase into organic phase where the reaction takes place. This is Phase Transfer Catalysis (PTC) process. On the other hand, it is likewise essential that the transferred active ion pair remains in an active form for necessary phase transfer catalytic action, and that it is reclaimed during the reaction in the organic. PTC is nowadays a broadly used process for organic synthesis due to its various merits such as its selectivity, simplicity, mild operating conditions, inexpensive catalyst, easily available catalyst, reduced consumption of organic solvent, raw materials, easily available bases for anion generation and enhanced rate of reaction.

1.7.1 Mechanism of Phase Transfer Catalysis:

The mechanism of the PTC was best described by Stark et al.; (1970) where a quaternary onium halide present in the aqueous phase (Q+X-) go through anion exchange with the anion (Y-) of the reactant (MY) present in the aqueous phase. The ion-pair formed (Q+Y-) is able to pass the liquid-liquid interface because of its lipophilic nature and goes from the interface into the organic phase, this step is the phase transfer. Since the anion of the ion-pair in the organic phase is nucleophilic, it go through a nucleophilic substitution reaction with the reagent (RX) forming the product (RY).

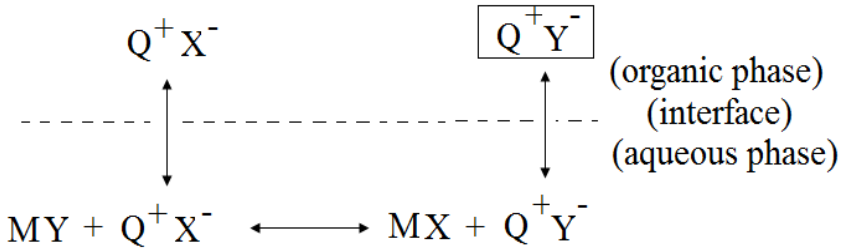


Figure 1.4: Stark's Mechanism

The catalyst then proceeds to the aqueous phase and in this way the cycle goes on. Fig.1.4 shows actual mechanism of PTC. This mechanism is used only when catalyst is hydrophilic in nature. Sometimes it may possible that PT catalyst is so lipophilic in nature that it can't dissolve in aqueous phase. In this case, anion exchange of nucleophile with catalyst takes place at or near the interphase. This mechanism was given by Brandstorm Montanari is also known as interfacial mechanism shown in fig. 1.5.

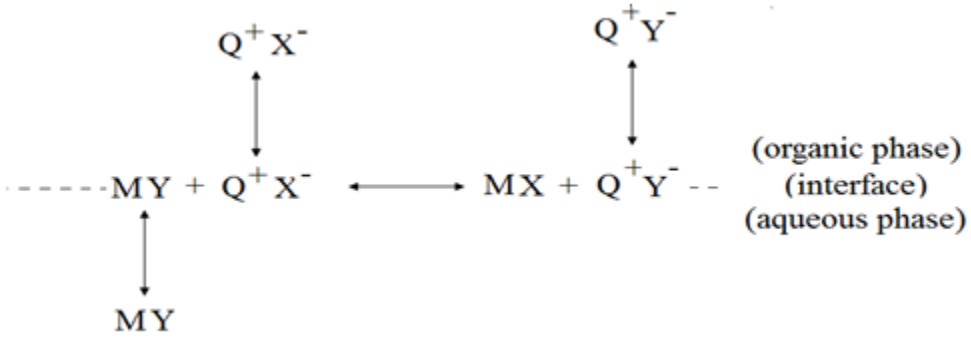


Figure 1.5: Bransdstorm Montanari Mechanism

1.7.2 Major classification of PTC:

PTC reactions are categorized into two categories: soluble and insoluble Phase Transfer Catalysis. Each category is again further carved up into a number of classes. Depending upon the physical form of the phases, PTC systems generally composed of, as shown in fig 1.6. To discuss the whole major classification is quite lengthy. So briefly, let us discuss the classification tree of PTC to one by one starting from soluble PTC.

The soluble phase transfer catalysis (Soluble PTC) is again classified as liquid-liquid phase transfer catalysis (L-L PTC), solid-liquid phase transfer catalysis (S-L PTC) and gas-liquid phase transfer catalysis (G-L PTC). The nucleophile (M+Y-) is dissolved in an aqueous phase in the case of L-L PTC but in the case of S-L PTC, it is solid suspended in the organic phase. In L-L systems more applications have been reported regarding PTC but sometimes S-L are also used in order to escape undesirable side reactions like hydrolysis to increase selectivity of product. There are basically two mechanisms, namely, interfacial and extraction, which are used to describe the L-L PTC depending on the lipophilicity of the quaternary cation. Stark's extraction mechanism is applied to low lipophilic catalysts and the mechanism has already been mentioned above. The interfacial phenomenon allows the catalysts to remain in the organic phase only owing to their high lipophilicity. In this phase, anions are also exchanged across the liquid-liquid interface.

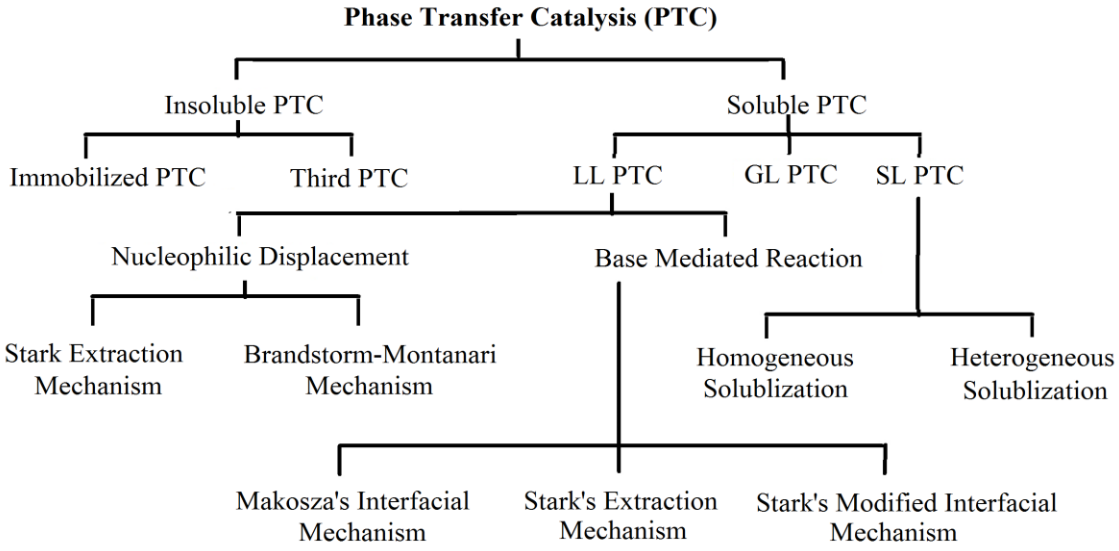


Fig 1.6: Schematic diagram of classification of PTC

In S-L PTC, (Starks and Liotta, 1978, Yadhav and Sharma 1981), two mechanisms have been proposed. One among the two is appropriate for conditions in which there is finite solubility in the inorganic salt in the given solvent. There is no direct reaction between the catalyst and the solid surface. And the second mechanism is functional in various situations where the inorganic salt is either soluble or insoluble in negligible proportions in the organic solvent and there is direct

reaction between the catalyst and the solid surface. This whole mechanism is known as homogeneous and heterogeneous solubilisation (Melville and Goddard). Furthermore, an increase in rate of reactions due to less amount of water in solid-liquid phase is termed as omega phase. The two distinct mechanisms are shown in the fig 1.7.

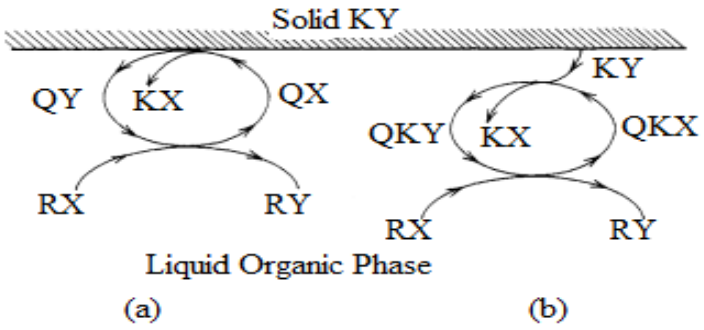


Figure 1.7: Mechanisms for Solid-Liquid are
(a) Heterogeneous solubilization (b) Homogeneous solubilization

G-L PTC involves the utilization of phase transfer catalyst in gas-liquid-solid systems. In this system, the organic substrate that remains in a gaseous form, is allowed to pass over a bed comprising of the inorganic reagents which are layered with a phase transfer catalyst in its melted state. But extraction and regaining of the PT catalyst from the organic phase becomes very expensive and difficult process because it gets almost dissolve in the organic phase and most of the times it is treated as waste. If it becomes possible to inhibit the PT catalyst to a third insoluble phase, whether it is liquid or solid, then the separation step can be carried away easily without any difficulty. The commonly used immobilized phase transfer catalysis is tri-phase system and third liquid PTC.

1.7.3 Types of phase transfer catalyst

Many varieties of PTC are available, such as phosphonium salts and quaternary ammonium salts, crown ethers, cryptands, ionic liquid, polyethylene glycol, etc. Out of these, the quaternary ammonium salts are widely used in the industry. PEG is the most economical while cryptands and

crown ethers are extremely costly among the usually used PT catalysts. PEG'S, cryptands, crown ethers and ionic remains steady at higher temperatures (150-200ºC). One should keep in mind that various applications of phase transfer catalysis require temperatures ranges between 50-120 ºC and quaternary onium salts remains active, steady, and is broadly appropriate under these specified conditions. But PEG's, crown ether and cryptands have higher stability to basic conditions as compared to quaternary onium salts but have some disadvantages.

Table 1.4: Several commonly used PT catalysts (Sanjeev D. Naik and L. K. Doraiswamy)

Catalyst	**Cost**	**Stability and Activity**	**Use and Recovery of Catalyst**
Ammonium Salts	Economical	Moderately stable under normal up to 100º C. Moderately active.	Broadly used & recovery is comparatively difficult.
Phosphonium Salts	Expensive than ammonium salts	More stable thermally as compared to ammonium salts, but not much stable under basic conditions.	Widely used but recovery is difficult to some extent.
Crown Ethers	Expensive	Stable and highly active both under usual conditions and also at higher temperature between 150 to 200 ºC.	Frequently used and regaining of the catalyst is difficult and affect environment due to its toxic nature.
Cryptands	Expensive	Stable and highly reactive, except in the presence of strong acids.	Used sometimes despite of high cost and toxic nature, due to higher reactivity.
Polyethylene glycol	Low-cost	More stable than quaternary ammonium salts, but lower activity.	Often used. It can be in use where larger amounts of catalyst creates no complications. Comparatively easy to recover.

Moreover, the separation and recovery of catalyst are also important challenge. Solid phase transfer catalyst,commonly recognised as reusable reagents have attracted growing attentions, by reason of their specific advantages, such easily recovering and reusing of the catalyst.

1.7.4 Choice of Immobilized PTC (Tri-phase catalysis):

Over insoluble PTC, the conventional soluble PTC has one major drawback of being non-recoverable and non-reusable from the liquid phase. Although several chemical separation processes, e.g. distillation or extraction, are available. But it can be difficult to separate the catalyst from the product through these processes and may considerably affect the monetary value as well as product purity. To overwhelm this primary problem, immobilized phase transfer catalyst on a solid support such as a polymeric resin or inorganic solid can be preferred and implement. This method is widely known as tri-phase transfer catalysis.

1.7.5 Tri-phase transfer catalysis (TPC):

In TPC, the catalyst distribution in the reaction system is more restricted since the active sites of the catalyst are immobilized on the solid support. Reactants present in both organic and aqueous phases need to transfer from their corresponding phases to the surface of the catalyst to contact the catalytic (active) sites. The activity of tri-phase catalyst, thus, can be summarized stepwise as:

a. Mass transfer of reactants from bulk liquid phase to the surface of the catalyst.
b. Diffusion of the reactant molecules from the surface of the catalyst particle to the active sites inside the porous particle.
c. Intrinsic reactivity of reaction at the active sites.

These external and intra-particle mass transfer requirements can significantly affect the rate of reaction; so it is normally supposed that tri-phase catalysts possess lower reactivity than in biphasic reaction systems. On the other hand, there are exceptional cases stated in the literature which shows higher reactivity of the tri-phase catalysis. Tundo et al.; (1989) reported that catalysts made by immobilization of onium salts on inorganic supports (silica and alumina) allow high nucleophilic

activity in bromide displacement on octylmethanesulfonate of which result in higher rate of reaction than for the same reaction in a homogeneous phase.

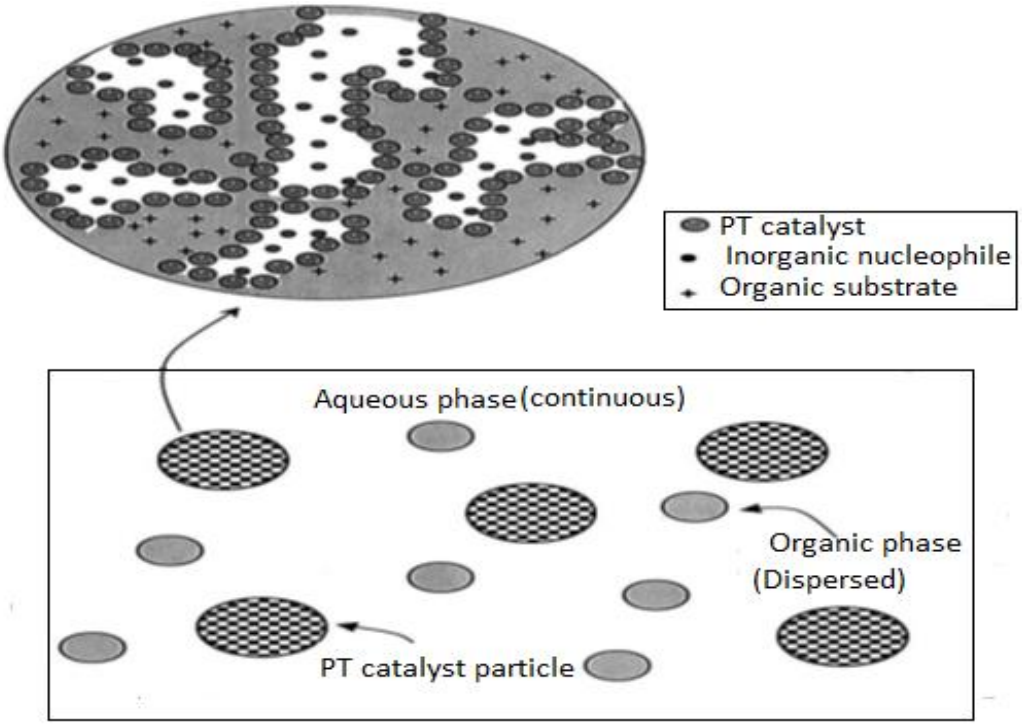


Fig 1.8: Activity of liquid-liquid-solid tri-phase catalysis

1.7.6 Catalyst used in tri-phase catalysis:

Most commonly used catalyst in tri-phase catalysis is ion exchange resin or Amberlite IR-400. An ion-exchange resin also known as ion-exchange polymer is an immiscible support structure or matrix, generally in the form of small beads and in the range of 0.5 to 1 mm diameter. The colour of the resin is white or yellowish and is fabricated with an organic polymer substrate. High surface area of the catalyst beads are due to its porous nature which helps the reaction to takes place effectively. The trapping of ions take place with releasing of other ions; therefore the process is known as ion-exchange. Variety of ion-exchange resin are available in the market. Most of the commercially used resins are usually of polystyrene sulfonate.

When the application is being concerned, ion-exchange resins are generally utilized in various processes like separation, purification, and decontamination. Water softening and water purification are among the most common examples. In various cases, ion-exchange resins were found to be more flexible replacement for the use of natural or artificial zeolites. In the method of

biodiesel filtration, ion exchange resins are found to be extremely effective. Furthermost usual ion-exchange resins depends on acrylic structure or cross linked polystyrene. To boot, in the case of polystyrene, cross linking is introduced by means of copolymerization of styrene and a few percent of divinylbenzene. The polymers which are non-cross linked are soluble in water. Cross linking reduces ion-exchange capability of the resin and extends the time required to carry through the ion exchange processes. The size of the particle too influence the resin parameters, smaller particles possess a larger outer surface, but then again cause larger head loss in the column procedures.

Fig 1.9: Ion exchange resin

There are four main kinds of ion exchange resin which have differences based on their functional groups:

(a) strongly acid nature , for example, sulfonic acid groups;
(b) strongly basic nature, for example, quaternary amino groups;
(c) weakly acidic nature, for example, carboxylic acid groups;
(d) weakly basic nature, for example, primary, secondary, and/or ternary amino groups.

Chapter 2

LITERATURE SURVEY

CHAPTER 2
LITERATURE SURVEY

2.1 USE OF AQUEOUS ALKANOLAMINES FOR THE REMOVAL OF H_2S:

Aqueous alkanolamines has a broad application in removing H_2S gas from gas streams generated in various industries. The amines that are proved to be of principal importance for gas purification are diethanolamine (DEA), monoethanolamine (MEA), and methyldiethanolamine (MDEA). The first used alkanalomine in industry was tri-ethanolamine (Bottoms et al., 1930) but due to certain disadvantages such as its low capacity, low reactivity and poor stability, it has been displaced largely. Aqueous MEA has been broadly used due to various properties such as high reactivity, ease of reclamation, low absorption of hydrocarbons, low solvent cost and low molecular weight (which results high solution capacity at moderate concentrations). MDEA has also been used because they are regenerable, they have high removal potential efficiencies and their ability to remove either H_2S or both CO_2 and H_2S is high (Zicarai et al., 2003) but its cost is high as compared to MEA. Several researchers studied the equilibrium solubility of pure H_2S (Lawson et al., 1976; Lee et al., 1976; Isaacs et al., 1980), mixture of acid gases (H_2S and CO_2) (Lee et al., 1976; Lawson et al., 1976; Isaacs et al., 1980), and the mathematical portrayal of the experimental solubility data for H_2S, CO_2 and mixture of CO_2 and H_2S (Austgen et al., 1989; Weiland et al., 1993; Al-Baghli et al., 2001; Kaewsichan et al., 2001) using aqueous MEA.

2.2 LIQUID-LIQUID PHASE TRANSFER CATALYSIS:

Y. B. Jadhav and G. D. Yadav (2003) studied the reduction of para-chloronitrobenzene using sodium sulphide under the various modes of Phase Transfer Catalysis such as Liquid-Liquid, Liquid-Solid and Liquid-Liquid-Liquid PTC processes. The influence of co-catalyst in intensification of rate of Liquid-Liquid PT catalysed reaction was also studied by them in reference to produce p-chlorophenyl acetonitrile in presence of Tetrabutylammoniumbromideas a Phase Transfer catalyst and KI as a co-catalyst. 100% selectivity of product was obtained due to co-catalyst. Kinetics of reaction between benzyl bromide and sodium benzoate in L-L system catalyzed by alsiquat 336 at 70 °C for 3 h of reaction using chlorobenzene as a solvent was studied

by Yang H., Lin C. (2003). Product yield obtained was 98%. Reduction of nitro toluene using $(NH_4)_2S$ as a reducing agent was carried out in toluene as organic solvent under L-LPTC in presence of Tetrabutylammoniumbromide. 100% selectivity of toluidine was found. (Pradhan N.C., Maity S.K., Patwardhan A. V.; 2006) Wang M. (2007) studied kinetics of Phase Transfer Catalysis etherification of 4, 4'-bis (chloromethyl)-1,1'-biphenyl with C_6H_6O i.e. phenol in alkaline solution of KOH/organic solvent as a two phase medium. Kinetics and mechanism of quaternary ammonium salt as a Phase Transfer Catalyst for thiophene oxidation was observed by Zhao D, Ren H. (2007). Different catalyst with ultrasound was employed and quaternary ammonium salt was found to be best with 94.67% desulfurization rate. The reactions of para-chlorobenzyl chloride and benzyl chloride with sodium sulfide produces dibenzylsulfide and bis (p-chlorobenzyl) sulfide, which are significant in the commercial field. These are called diarylsulfides and finds several uses as supplementary for extreme pressure lubricants, as antiwear additives for motor oils, as stabilizers for photographic emulsions, in refining and recovery of precious metals, and in different anticorrosive formulations. (Pradhan and Sharma, 1990). Maity S.K., Sen S., Pradhan N. C. (2007) used TBAB as phase transfer catalyst and produced DBS by reacting BC and aqueous ammonium sulphide**.** Sen S., Pradhan N.C. and Patwardhan (2011) also studied and examined the reaction of BC with H_2S rich MEA solution under L-L PTC and found that if the ratio of MEA/H_2S is higher it favours the formation dibenzylsulfide and if the ratio is lower it favours the formation of BM. TBAB was used as PTC.

2.3 SYNTHESIS OF DIBENZYLDISULFIDE:

Extensive research has been performed for the preparation of disulfide by various researchers by the application of PTC. Depending on the reaction between sodium sulfide and sulfur using didecyldimethylammonium bromide (DDAB), Sonavane et al., (2007) has developed a simple and convenient method for the preparation of symmetrical as well as asymmetrical cyclic disulfides using PT catalyst. Abbasi et al.; (2012) has introduced an effective and odourless preparation of disulfides from alkyl halides by the use of elemental sulfur and thiourea with sodium carbonate in wet PEG 200 at 40^0C. Further this procedure has also been extended for the synthesis of disulfides from alkyl tosylates at 70^0C.

Alternative ways for the preparation of disulfide has been suggested by Tajbakhsh et al.; (2004) where 2, 6-Dicarboxypyridinium chlorochromate has been found to be a methodical reagent for the conversion sulfides to sulfoxides and thiols to disulfides under neutral and anhydrous conditions in good to a worthy yields. At room temperature, the selective oxidation of thiols in the presence of sulfides is also observed with this reagent.

On converting alkyl halides to the disulfides, Polshettiwar et al.; (2004) found Benzyl-triethyl-ammonium tetra-cosathio-hepta-molybdate $[(C_6H_5CH_2N(Et)_3)_6Mo_7S_{24}]$ as a superior sulfur transfer reagent with a worthy yields under normal reaction conditions. The application of this reagent offers various advantages such as mild reaction conditions, economy process, easy preparation of the reagent and a convenient workup procedure. Also, this method provides a simple, versatile and general route for the preparation of a wide variety of disulfides due to its solubility.

Recently, on synthesizing the symmetrical disulfides starting from thiols, Thurow et al.; (2011) have presented the results on the use of 1-n-butyl-3-methylimidazolium methylselenite, [bmim] $[SeO_2(OCH_3)]$. This method is general for aromatic, aliphatic, and functionalized thiols affording the disulfides in good to excellent yields after easy work up. The use of a microwave accelerates the reaction and the [bmim] $[SeO_2(OCH_3)]$ was reused for further oxidation reactions. Way back, Sonavane et al.; (2007) developed a one-pot, rapid and general method for the synthesis of symmetrical disulfides based on reaction of sulfur with sodium sulfide in the presence of didecyldimethylammonium bromide (DDAB) as a phase transfer catalyst is reported. Reaction with a variety of alkyl halides, at room temperature, afforded the disulfides in good to excellent isolated yields in a short period.

Ali at el.; (2002), have developed a simple, efficient, and mild procedure method for oxidizing thiols with molecular bromine on hydrated silica gel support for the conversion of thiols to the disulfides and dithiols to cyclic disulfides. The procedure utilizes organic media and does not require a base to neutralize HBr by-products to suppress acid promoted side reactions.

2.4 USE OF TRIPHASE CATALYST:

In the Liquid-Liquid PTC, the catalyst is generally not easy to recover so it is discarded causing load to the surroundings. The catalysts in L-L PTC are soluble in both the phases where

product in pure form could not be obtained. Therefore, the catalyst is eliminated by treating the organic phase of the system with large amount of water which is then sent to the effluent treatment plant. But, water washing decreases the overall yield of the product which is undesirable. Moreover, the separation of catalyst from the reaction mixture demands extraction, distillation and adsorption which consume high energy. Therefore, tri-phase catalysis is the best alternative to L-L-PTC where catalyst can be recover and reuse easily.

Pradhan et al.; (1992) have investigated the catalytic activity of some common tri-phase catalyst namely alumina and Amberlyst A27(Cl-), on the reaction of benzyl chloride and para-chlorobenzyl chloride with solid sodium sulfide. Dutta et al.; (1994) studied the reaction of phenol in alkaline solution and benzyl chloride dissolved in toluene along with polymer supported tri-n-butylphosphonium ion as phase transfer catalyst in a slurry reactor and mass transfer effect have been analysed with the standard theory of porous catalyst. The intrinsic reaction rate constant and diffusion co-efficient within the porous polymer particle are estimated. Yadav et al. ;(1997) studied the use of a novel catalyst based on heteropolyacid supported on clay, particularly dodecatungstophosphoric acid (DTP) catalyst have been found as reusable and efficient at high temperatures. Naik at el.; (2000), also prepared a clay supported phase transfer catalyst and used it for the preparation of benzoic anhydride from benzoyl chloride and sodium benzoate using clay-supported quaternary ammonium salts at 30 °C. The clay supported catalyst were more active than polymer supported catalyst here and 100% selectivity has been obtained.

Desikan et al.; (2000) also investigated on the esterification of benzyl chloride with aqueous sodium acetate with tributylmethylammonium chloride as catalyst and stated that the faster rate of reaction have been observed with the polymer-supported catalyst than its soluble analogue. Glatzer et al.; (2000) reported an assessment comparing the heterogeneous and homogeneous PT catalysts with different categories of PTC systems. It was possible to find out the conditions under which the polymer supported catalyst enhanced the reaction system distinctly better than its soluble counterpart. Holger et al.; (2002) further reported the kinetic model for triphase catalytic systems which is based on the traditional kinetic mechanisms of the Langmuir-Hinshelwood and Eley-Ridealtype's modified to suit the special case of catalysis by solid supported PT catalyst (i.e. TPC). The synthesis of octyl acetate from reaction between octyl bromide and potassium acetate has been used to test the validity of this model. This model could

predict whether a triphase catalytic system is limited by the organic reaction step, ion-exchange step, or a combination of both the steps.

Joshi et al.; (2001), reported the usability of solid acid catalyst for the synthesis of tert amyl methylether (TAME) by reacting tert amyl alcohol and methanol. Yadav et al.; (2007) studied the facts of formation of a third phase in biphasic reaction where Liquid-Liquid-Liuid Phase Transfer Catalysis increases the conversion and selectivity. The confirmation have been made by the reaction between phenol and benzyl chloride under Liquid-Liquid PTC. Maity et al.; (2008) have reported the reduction of p-nitrotoluene by aqueous ammonium sulfide with serelite SRA400 as catalyst using triphase catalysis reaction and established that reduction rate of of PNT is proportional to the square of the concentration of sulfide and to the cube of the concentration of PNT. Additionally, enhancement of the rate have also been observed with the once used catalyst due to the presence of elemental sulfur on the surface of the catalyst.

Wang et al.; (2010), further reported the various type of quaternary salt type tri phase catalyst on the esterification reaction of benzyl chloride with sodium acetate. Some important observation have been reported as:

(1) Among quaternary phosphonium and quaternary ammoninum type TPC, ammonium type have the higher activity than other type catalyst

(2) Triphase Catalyst which is highly lipophilic, substitution takes place at N atom and their catalytic activity is high.

(3) Triphase Catalyst links the quaternary onium salt group to the matrix microsphere because of its longer shaper arm and shows high catalytic activity

(4) The hydrophilic and hydrophobic property of the TPC is affected by the bonding density of quaternary onium salt group and hence influences the catalytic activity.

Chapter 3

EXPERIMENTAL SETUP

Chapter 3

EXPERIMENTAL SETUP

3.1 CHEMICALS:

Preparation of H_2S rich mono ethanol amine

- Sulphuric acid from Merck Pvt. Ltd., Mumbai (98%)
- Iron Sulfide fused sticks for producing H_2S from Merck Pvt. Ltd., Mumbai
- Silicon high vacuum grease from RFCL Limited, New Delhi
- Monoethanolamine from Loba Chem ie Pvt. Ltd., Mumbai (99%)

Estimation of sulphide content

- Sodium thiosulphatepentahydrate (purified) from Merck Pvt. Ltd. (≥99%)
- Potassium iodate GR from Merck Pvt. Ltd. (≥99.5%)
- Sodium hydroxide pellets (purified) from Merck Pvt. Ltd. (≥97%)
- Starch soluble GR from Merck Pvt. Ltd.
- Potassium iodide GR from Merck Pvt. Ltd. (99.8%)

Preparation of Organic Phase

- Toluene from RFCL Limited, New Delhi (≥99.5%)
- Benzyl chloride from Merck (India) Ltd., Mumbai (≥99%)
- Acetone from RFCL Limited, New Delhi (99.5%)

Catalyst

- Amberlite 400IR

3.2 PREPARATION OF H_2S -RICH AQUEOUS ALKANOLAMINE

To prepare H_2S-rich aqueous monoethanolamine (MEA), about 30- 35 weight% solution of aqueous alkanolamine was developed by first adding a suitable standard of required alkanolamine in distilled water. The H_2S gas then produced in the Kipp's apparatus as shown in fig. 3.1, was bubbled through this aqueous alkanolamines solution in a gas bubbler of 250 mL standard. In laboratory scale, H_2S gas was prepared in Kipp's apparatus by reacting FeS sticks with H_2SO_4. 1 molar concentration of H_2SO_4 was taken and the reaction was carried out in Kipp's apparatus is as shown below.

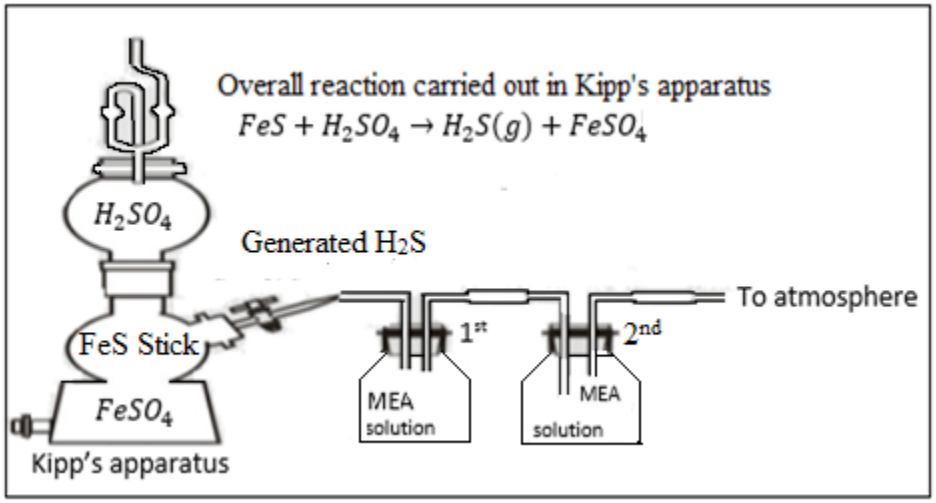


Figure 3.1: Representation of diagram for the absorption of H_2S in MEA solution.

The reaction of H_2S with alkanolamine is exothermic in nature (Kohl and Nielsen, 1997), so the gas bubbler holding aqueous alkanolamine was set engrossed in an ice water tub to avoid the oxidation of sulfide and the formation of disulfide. The H_2S gas coming from the first bubbler was sent to another bubbler containing approximately 1M MEA solution. The outlet of this bubbler was exposed to air. The bubbling of the gas was continued till the required sulfide concentration was attained in the aqueous alkanolamines.

3.3 EQUIPMENT

All the reactions were carried out in the batch reactor, in an entirely baffled automatically agitated glass reactor of 250 cm^3. At a height of 1.5 cm from the bottom of reactor a six-bladed glass impeller of 2.0 cm-diameter is located. The provision of speed regulation is also available. The impeller was provided in order to stir the reaction mixture. The reactor assembly was held back in a constant temperature water bath whose temperature could be controlled within ±1°C. The diagram of the experimental arrangement is as shown below.

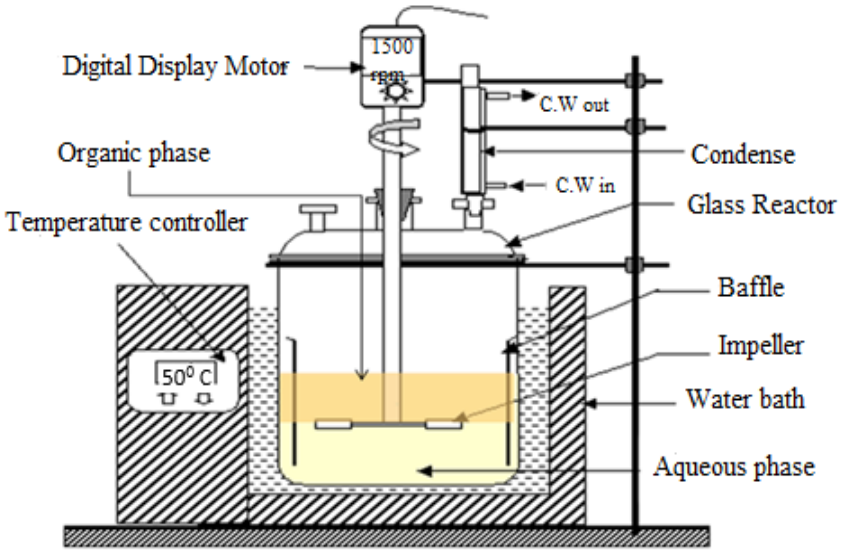


Figure 3.2: Representation of the diagram of the batch reactor

3.4 EXPERIMENTAL PROCEDURE

In the experiment, the three necked batch reactor was loaded with 50 ml of aqueous phase with known sulfide concentration. The reactor is well stirred up to attain a steady state temperature. After reaching that temperature, 50 ml of the organic phase containing a definite amount of organic reactant (benzyl chloride) and phase-transfer catalyst (Amberlite IR400) is loaded and then the reactor mixture is dissolved in toluene to make an organic solution. Toluene is used as the organic solvent. Now, the organic solutions are mixed with the aqueous solution in a volumetric flask of 250-mL. In order to initiate the reaction, the flask was kept engrossed in an isothermal water bath. At a constant speed, the reaction mixture was stirred. Now, after stopping the agitation of the reaction mixture and letting to separate the phases, about 0.1 ml of the organic phase sample, of the organic layer was taken out with the help of a pipette, at a fixed time interval of 5-480 min. The pipette was then put into the test tubes. This sample i.e. 0.1 mL was taken out from the necked batch reactor and then placed the sample into the glass vials.

3.5 METHOD OF ANALYSIS:

3.5.1 Determination of Sulfide Concentration

Determination of initial sulfide concentration was done by standard iodometric titration method (Scott, 1966) as given below.

Preparation of standard (0.025 M) KIO_3solution:

5.3 gm of $KIO_3$was weighed accurately and dissolved in distilled water and was built up to 1 L in a graduated volumetric flask.

Preparation of standard (0.1 M) sodium thiosulfate solution:

25 gm of $Na_2S_2O_3.5H_2O$ crystals was weighed and dissolved in distilled water and made up to 1 L in a graduated volumetric flask with distilled water. Approximately, 0.1 g of sodium carbonate or three drops of chloroform was added to this solution to retain the solution for more than a few days.

Standardization of sodium thiosulfate solution by standard potassium iodate solution:

25 mL of 0.025M KIO_3solution was taken and 1 gm (excess) of potassium iodide (KI) added to it followed by 3 mL of 1 M sulfuric acid. Thiosulfate solution was taken in the burette to titrate the liberated iodine (I_2).When the solution colour changes to pale yellow, it was diluted to 200 mL with distilled water. A few drops of starch solution were added, and the titration was carried on until the colour transformed from blue to colourless. The chemical reaction involved in this titration is given below.

$$\boldsymbol{KIO_3 + 5KI + 3H_2SO_4 \leftrightarrow\ 3I_2 +\ 3H_2O + 3K_2SO_4}$$

$$\boldsymbol{2Na_2S_20_3 + I_3 \leftrightarrow\ Na_2S_4O_6 + 2NaI}$$

1 mole of KIO_3≡ 3×2 mole of $Na_2S_2O_3$

Therefore, Strength of Thiosulfate solution=$\frac{6*strength\ of\ KIO_3*volume\ of\ KIO_3}{volume\ of\ thiosulfate\ consumed}$

Estimation of sulfide concentration:

Hydrogen sulfide and soluble sulfides can be found by oxidation with potassium iodate in an alkaline medium. 15 cm^3 of standard (0.025M) potassium iodate solution was taken in a conical flask. 10 cm^3 of sulfide solution containing about 2.5 mg of sulfide was then added to it. After that 10 $cm^3$of 10M sodium hydroxide solution was also added to it. The mixture was boiled mildly for about 10 minutes, cooled, and 5 $cm^3$of KI solution and 20 $cm^3$of 4M sulphuric acid solution were added to it. The liberated iodine was titrated, which was equivalent to the unused potassium iodate, with a standard 0.1M sodium thiosulfate in the common way. The potassium iodate in the alkaline medium oxidizes the sulfide to sulfate as given by the following reaction. For sulfide solution having sufficiently high sulphide concentration, suitable dilution was prepared before the estimation of sulfide by abovementioned procedure.

$$4IO3^- + 6OH^- + 3S^{2-} = 3SO4^{2-} + 4I^- + 6H2O$$

4 mole of IO_3^- ≡ *3 mole of* S^{2-}

$$H_2S\boldsymbol{concentration} = \left\{\left[(15 * S_{iodate}) - \frac{(V_{\text{thiosulfate}} * S_{\text{thiosulfate}})}{6}\right] * \frac{3}{4} * \frac{N_d}{10}\right\}$$

where, S_{iodate}= Strength of KIO_3

$V_{thiosulfate}$= Volume of thiosulfate

$S_{thiosulfate}$= Strength of thiosulfate

N_d= Number of times of dilution

3.5.2 Analysis of Organic Phase:

All organic samples were analyzed by the help of Gas Liquid Chromatography (GLC) using a 30m long and 0.25mm in diameter capillary packed column. A Flame Ionization Detector (FID) was used with nitrogen as the carrier gas. The nitrogen gas flow rate is kept at 25ml/min, injection temperature was maintained at 250 ºC and detector temperature was 300 ºC. Oven program is put in a way that oven is kept at 50 ºC for 2min and then it is heated up to 280 ºC at the rate of 20 ºC/min and 300 ºC is maintained for 4 min.

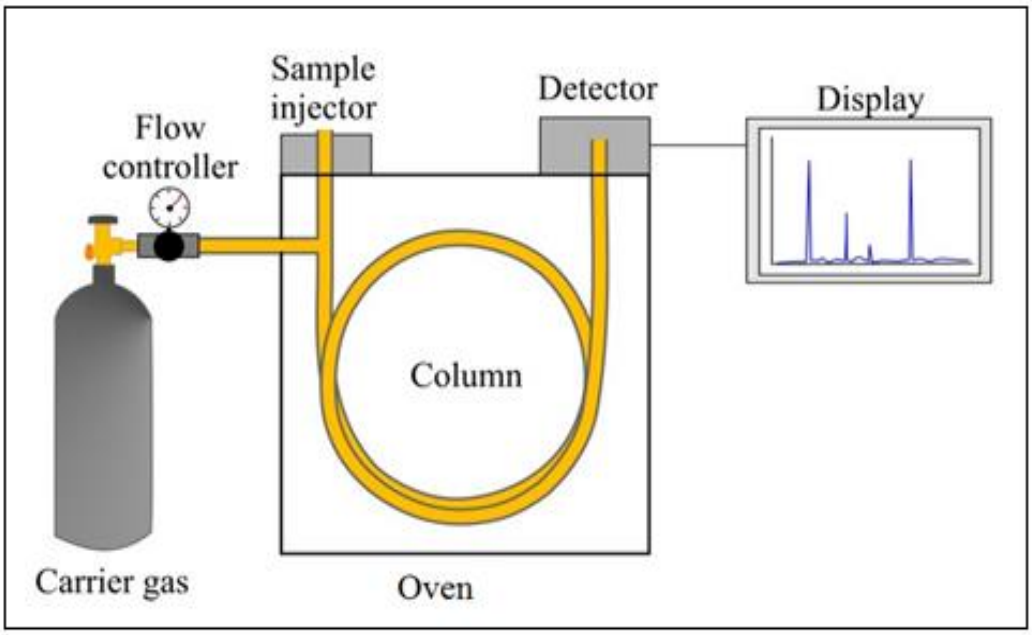


Figure 3.3: A Gas Chromatography

The GC Spectra of present system at the beginning and end of synthesis is shown in figure 3.4 (i) and (ii) respectively. The figure shows that the components are leaving with different retention time depending on their relative volatility with different area of chromatogram. Toluene has constant area chromatogram as it is not participating in synthesis reaction but decrease in BC chromatogram area is observed with the course of reaction and subsequently formation of DBDS is notice with increase in its chromatogram area with increase in reaction time.

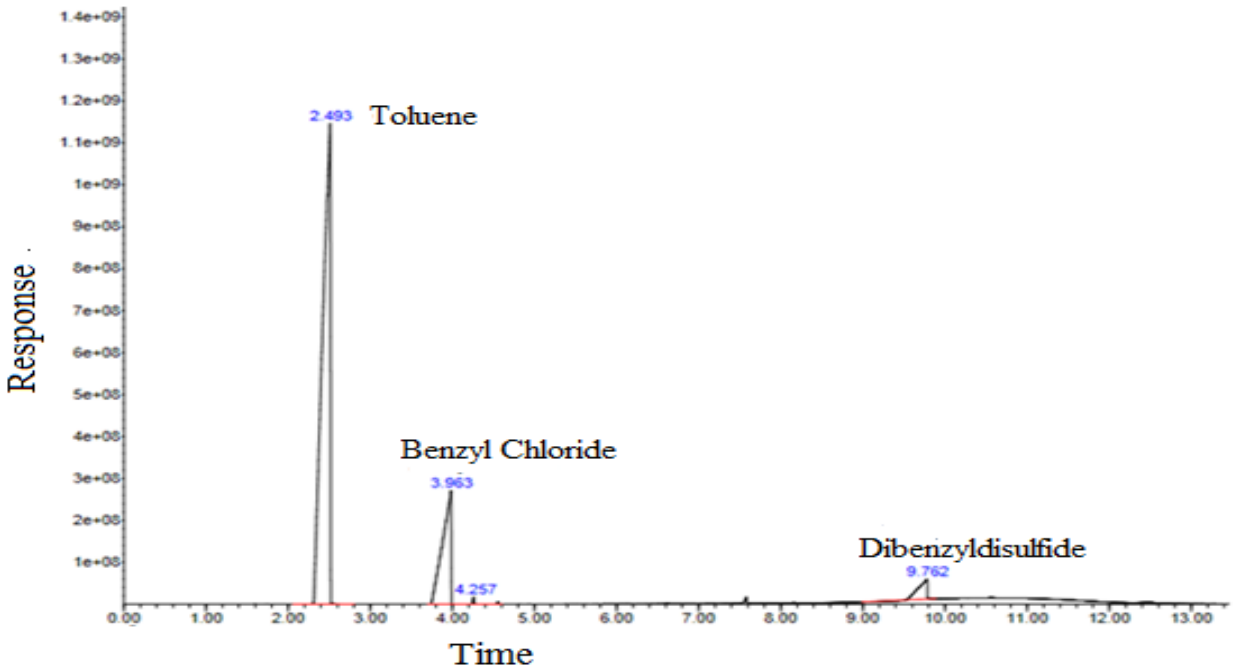


Figure: 3.4: (i) Chromatogram at 5min

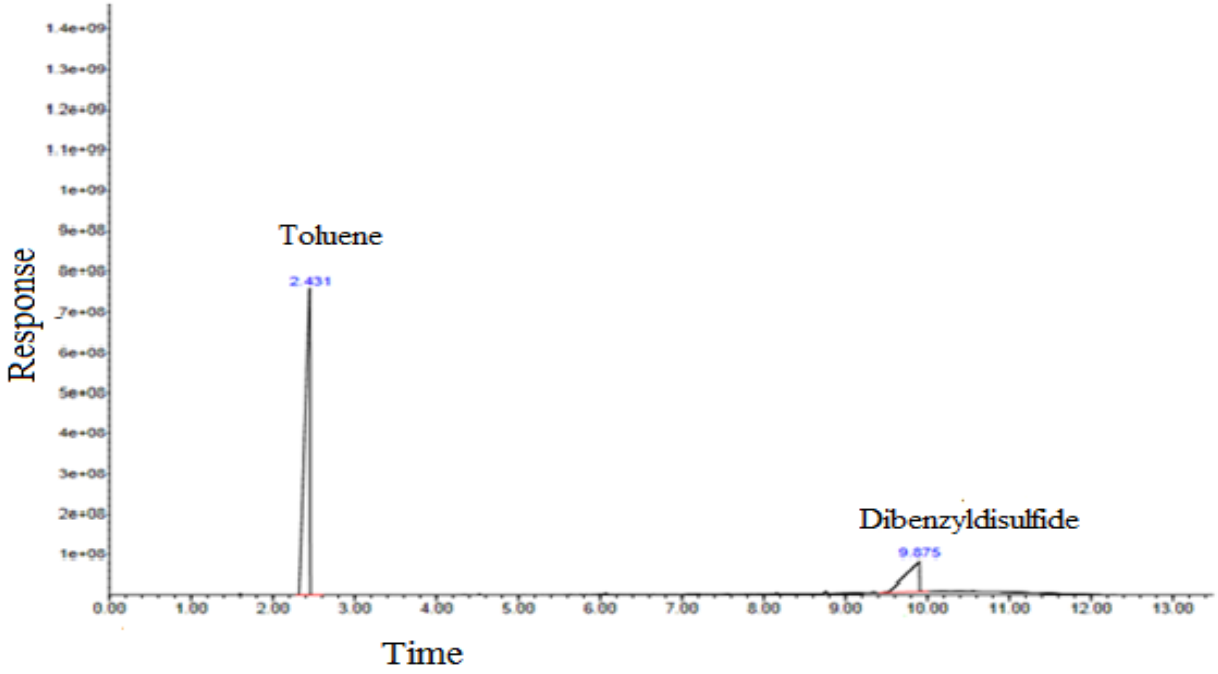


Figure 3.4: (ii) Chromatogram at 480min

Chapter 4

REACTION OF BENZYL CHLORIDE WITH H_2S -RICH AQUEOUS MONOETHANOLAMINE UNDER LIQUID-LIQUID-SOLID PHASE TRANSFER CATALYSIS

Chapter 4

REACTION OF BENZYL CHLORIDE WITH H_2S -RICH AQUEOUS MONOETHANOLAMINE UNDER LIQUID-LIQUID-SOLID PHASE TRANSFER CATALYSIS

4.1 INTRODUCTION

Value added products like DibenzylDisulfide (DBDS) and Dibenzylsulfide (DBS) are formed in the present work by reacting benzyl chloride with H_2S rich aqueous monoethanolamine in the presence of sulfur powder and phase transfer catalyst. Disulfides are significant compounds owning inimitable and varied properties in the biochemical as well as synthetic fields. Several bioactive molecules predominantly contain large disulphide linked groups. Technologically, disulfides find varied uses as vulcanizing agents for elastomers and rubbers which provides them good tensile strength. The disulfide moieties forms in proteins and is set up in a mixture of small naturally obtained products and pharmacologically active compounds. Additionally, cyclic and acyclic disulfides is advantageous species in the production of biologically-active compounds in many pharmaceutical as well as agro-chemical intermediates (Billard at el.; 1996, Nuzo et al.; 1983). Moreover, DibenzylDisulfide (DBDS) find their application in manufacturing corrosive inhibitors, fragrance compounds, high pressure lubricant additives, organic compounds and many more.

Disulfide as well as polysulfide anions are effortlessly attained by mixing aqueous solutions of S^{2-} with sulfur. Numerous investigative procedures were recently established to assess the polysulfide distribution in a number of sulfur/sulfide mixtures. In a general method, benzyl chloride in an organic solvent was agitated with aqueous sodium sulfide and sulfur in the existence of phase transfer catalysts at room temperature. In the present study, the reaction was held out in batch mode under tri-phase conditions (liquid-liquid-solid) both with and without of phase transfer catalyst (PTC) Amberlite IR 400 and in the presence of sulfur powder. A putative reaction mechanism were proposed where, in the presence of sulfur, aqueous hydrogen sulfide forms $(RNH_3)_2S_2$.The latter reacts with the phase transfer catalyst to form the ion pair Q_2S_2, which is transferred to the organic phase to react with the substrate to yield the dialkyl disulphide.

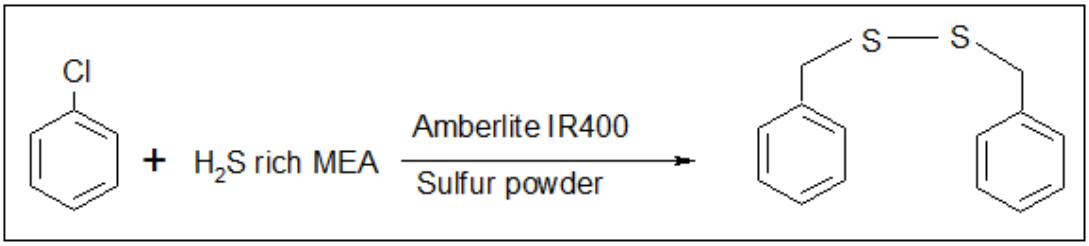


Figure. 4.1 Mechanism

Subsequently, the nature of the polysulfide anion in water ($S^{2-}x$ where x ¼ 2; 3; 4) can be obtained by adjusting the sulphide to sulfur ratio and it is concluded that tri, tetra and higher dialkylpolysulfides could be produced by means of the process described above. DibenzylDisulfide (DBDS), Dibenzylsulfide DBS and trisulfide were detected as the products from the reaction mixture by gas liquid chromatography (GLC). The selectivity of DBDS was maximized by changing several parameters such as stirring speed, temperature, sulfur powder loading, and aqueous sulfide concentration. Catalyst loading and concentration of benzyl chloride as discussed below in the respective sections. From the thorough survey on the various parameters of the reaction, an appropriate mechanism was built which could describe the progess of the reaction. Parametric studies have been accomplished following one-variable-at-a-time (OVAT) approach to take in the consequence of various parameters such as speed of agitation, temperature, aqueous sulfide concentration, catalyst loading and BC concentration on BC conversion and DBDS selectivity.

4.2 RESULTS AND DISCUSSION

4.2.1 Effect of Speed of Agitation:

The mass transfer along with the chemical reaction is essential in effecting the conversion on the rate of the three-phase reaction. In this study, to confirm the effects of mass transfer resistance of the reactants on the reaction phase, effect of the agitation speed on the conversion of benzyl chloride was varied in the range 1000-2000 rpm under the presence of PTC (Amberlite IR 400), as shown in Figure 4.2. It can be determined from the graph that there is a relatively less conversion at 1000 rpm compared to that at 1500 rpm and 2000 rpm. Eventually, the reaction rate at 1500 rpm is predominant while the mass transfer rate is negligible. Thus, the difference in conversion of benzyl chloride with stirring speed is so less that the mass transfer resistance turn out to be less significant and the reaction rate is held alone by the reaction kinetics. Consequently,

all further experiments were performed at a stirring speed of1500 rpm with the objective of ensuring the absence of mass transfer resistance.

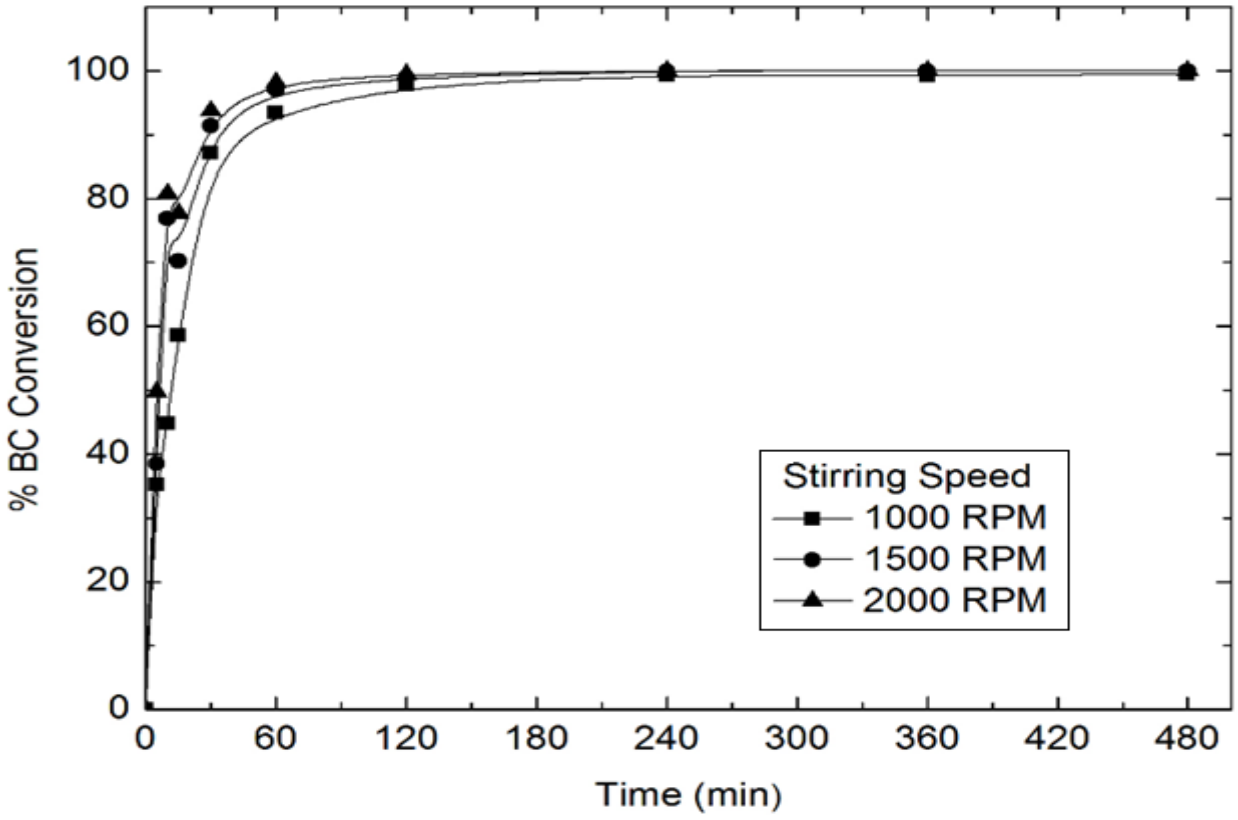


Figure 4.2: **Effect of speed of agitation**: Volume of Organic phase = 50ml; Volume of BC = 15ml; Volume of Aqueous Phase = 50ml; Catalyst loading= 5gm; Sulfide Concentration = 2.53kmol/m^3; MEA/H_2S mole ratio = 2.28; Temperature = 323 K; Sulfur loading= 3gm

4.2.2 Effect of elemental sulfur loading:

Elemental sulfur was loaded with H_2S rich monoethanolamine as an aqueous reactant for the synthesis of polysulfide. The colour of H_2S rich aqueous MEA changes from green to reddish brown. This colour change shows the formation of polysulfide ions (S_x^{2-}) where x can be 2, 3, 4, 5 depending on sulphur loading. The effect of this sulfur loading in DBDS synthesis is investigated by dissolving different concentration of sulfur powder in aqueous phase. At low concentration of sulfur around1 to 2gm, low selectivity of DBDS was noticed and it is nearly negligible in absence of sulphur powder as demonstrated in figure below.

It can be explained that at low sulfur concentration, hydrosulfide and sulfide ions are the dominating sulfide ions, giving unwanted side product BM and DBS over DBDS. With further increase in sulfur powder, polysulfide ions are formed in polysulfide synthesis, again giving low selectivity of DBDS as shown in figure below at 4 to 5 gm of sulfur. 3gm of sulfur is seen as an ideal reaction parameter giving 100% of DBDS.

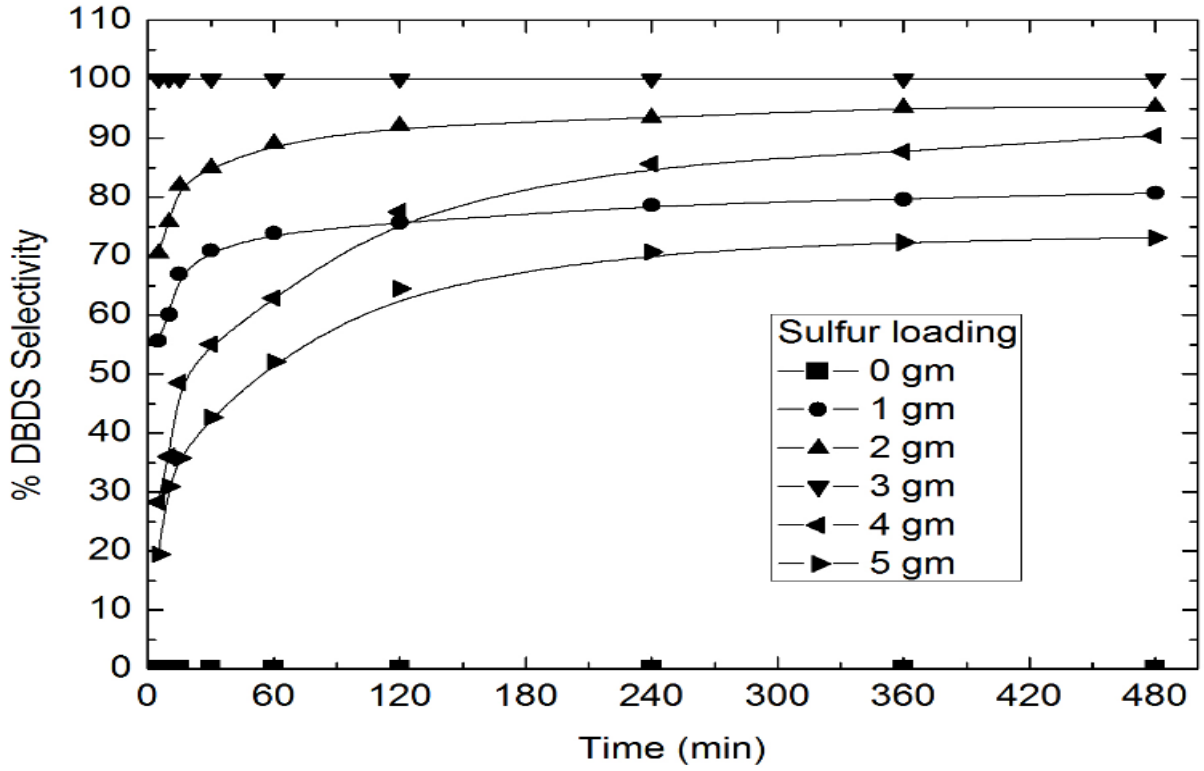


Figure 4.3: Effect of Elemental Sulfur loading: Volume of Organic Phase = 50ml; Volume of BC = 15ml; Volume of Aqueous Phase = 50ml; Catalyst loading= 5gm; Sulfide Concentration = 2.53kmol/m^3; MEA/H_2S mole ratio = 2.28; Stirring Speed =1500rpm; Sulfur loading=3gm; Temperature = 323 K.

4.2.3 Effect of Temperature:

Herein, the work elucidates the reaction of BC in presence of Toluene catalysed by a new resin catalyst Amberlite IR 400 in the presence of H_2S rich aqueous monoethanolamine under various reaction temperatures was studied under four different temperatures in the range 303-333K. Fig. 4.4 shows the effect of temperature on conversion of benzyl chloride. As expected, with the temperature increases as reaction rate of organic reaction increases as per the transition-state theory. That's why, increase in temperature uphold slow organic phase reactions in PTC

system. It is obvious that the reactivity (conversion) of BC increases as the temperature increases. In present synthesis, selectivity of desired product DBDS is always 100% at all temperature conditions. Since, the rate of reaction is directly proportional to the temperature, as the temperature increases, the reaction rate increases, thereby increasing the conversion of the reactant at higher temperature.

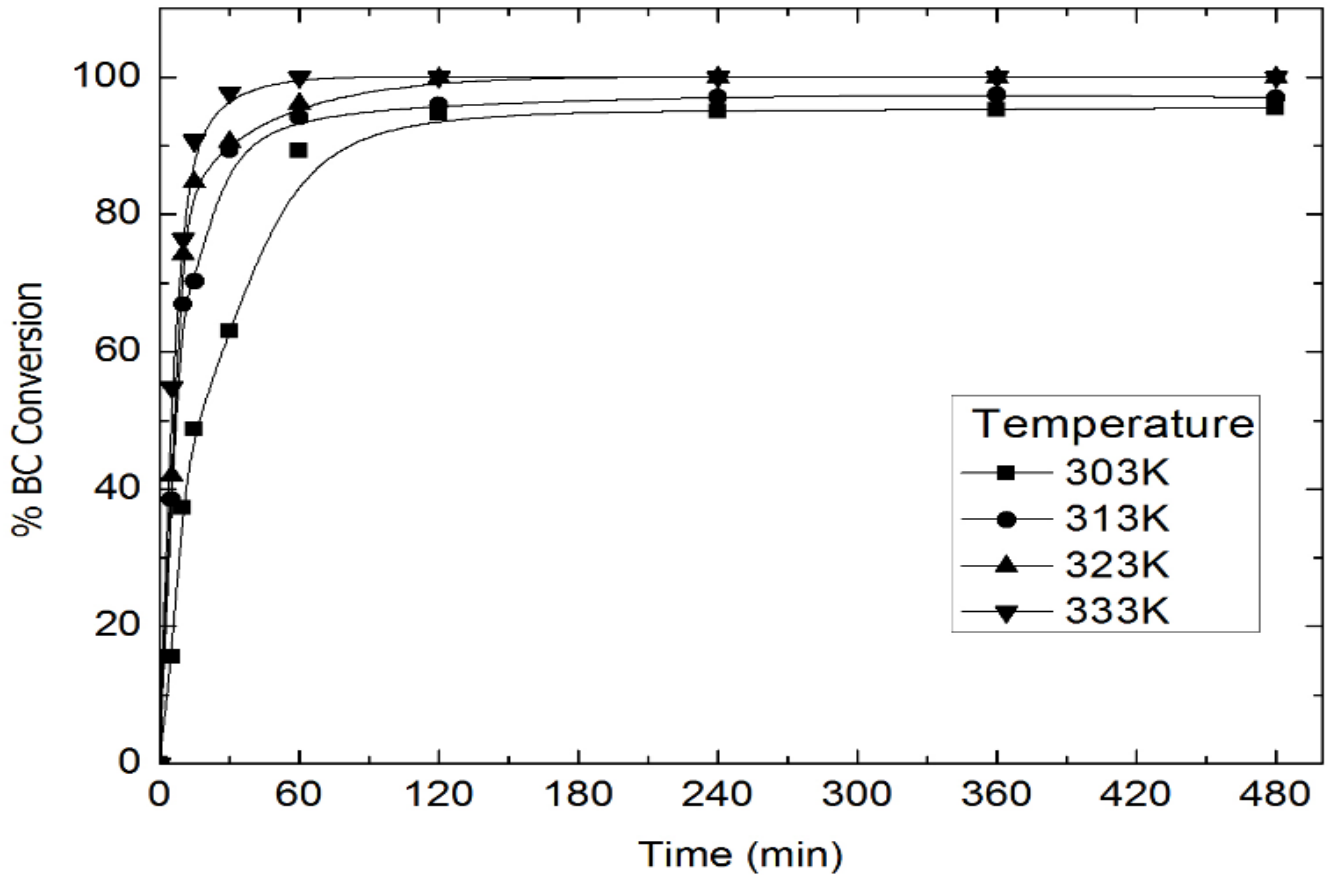


Figure 4.4: Effect of temperature: Volume of Organic Phase = 50ml; Volume of BC = 15ml; Volume of Aqueous phase = 50ml; Catalyst loading= 5gm; Sulfide Concentration = 2.53kmol/m^3; MEA/H_2S mole ratio = 2.28; Sulfur loading=3gm; Stirring Speed =1500rpm

Initially, reaction rate of benzyl chloride (BC) was found out at varied temperatures and an Arrhenius plot of –ln (initial rate) versus 1/T was prepared as indicated in Fig. 4.5.By calculation, the activation energy for the reaction of benzyl chloride was found from the gradient of the straight line as 22.4 KJ mol-1. The final confirmation of the controlled reaction could be achieved from the observed activation energy.

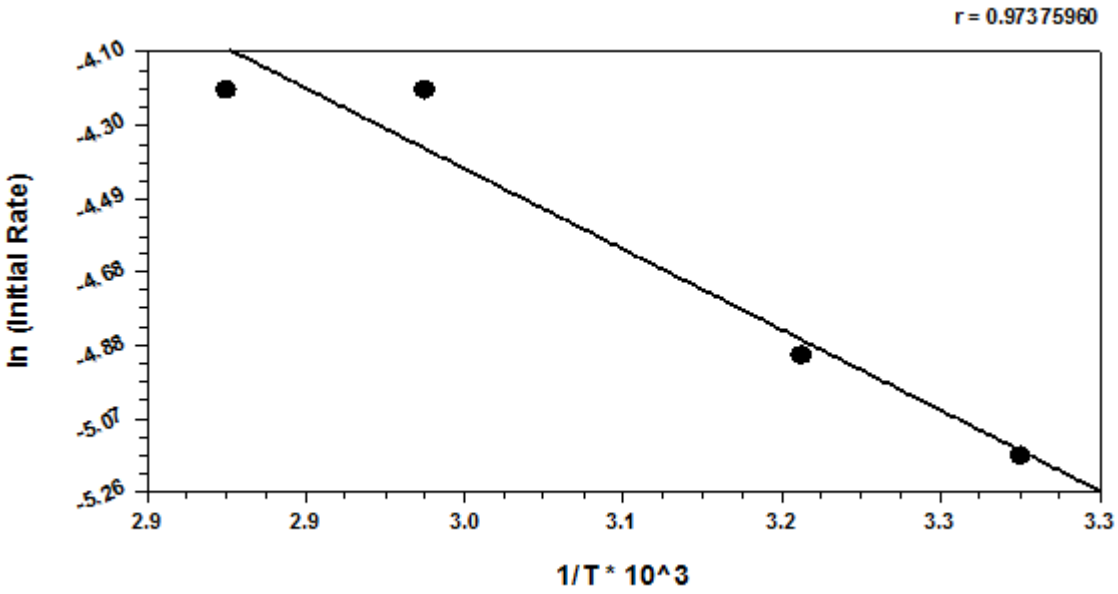


Figure 4.5: Arrhenius plot for Activation energy

4.2.4 Effect of catalyst loading:

The effect of catalyst loading was studied at five different catalyst concentrations in the range of 0.0- 0.58kmol/m^3as shown in Fig. 4.6. As the catalyst concentration increases, benzyl chloride conversion and reaction rate increases**.** Benzyl chloride conversion of 100 % was attained by increasing the catalyst concentration, whereas it was just about 45% in presence of catalyst even after 480 minutes of reaction. This demonstrates the significance of PTC in increasing the reaction rate.

The sulphide (S^{2-}) and disulphide (S_2^{2-})ions forms a pair of ions [(QSQ and ($Q_2S_2^{2-}$)] with quaternary cations [Q^+], and then moves to the organic phase thereby reacting with benzyl chloride. By increasing the concentration of the catalyst, more amount of ($Q_2S_2^{2-}$) ion pair is formed and moved to the organic phase to react with benzyl chloride to produce DBS and DBDS respectively. In present reaction condition, selectivity was almost 100% due to the presence of adequate amount of sulfur in aqueous phase.

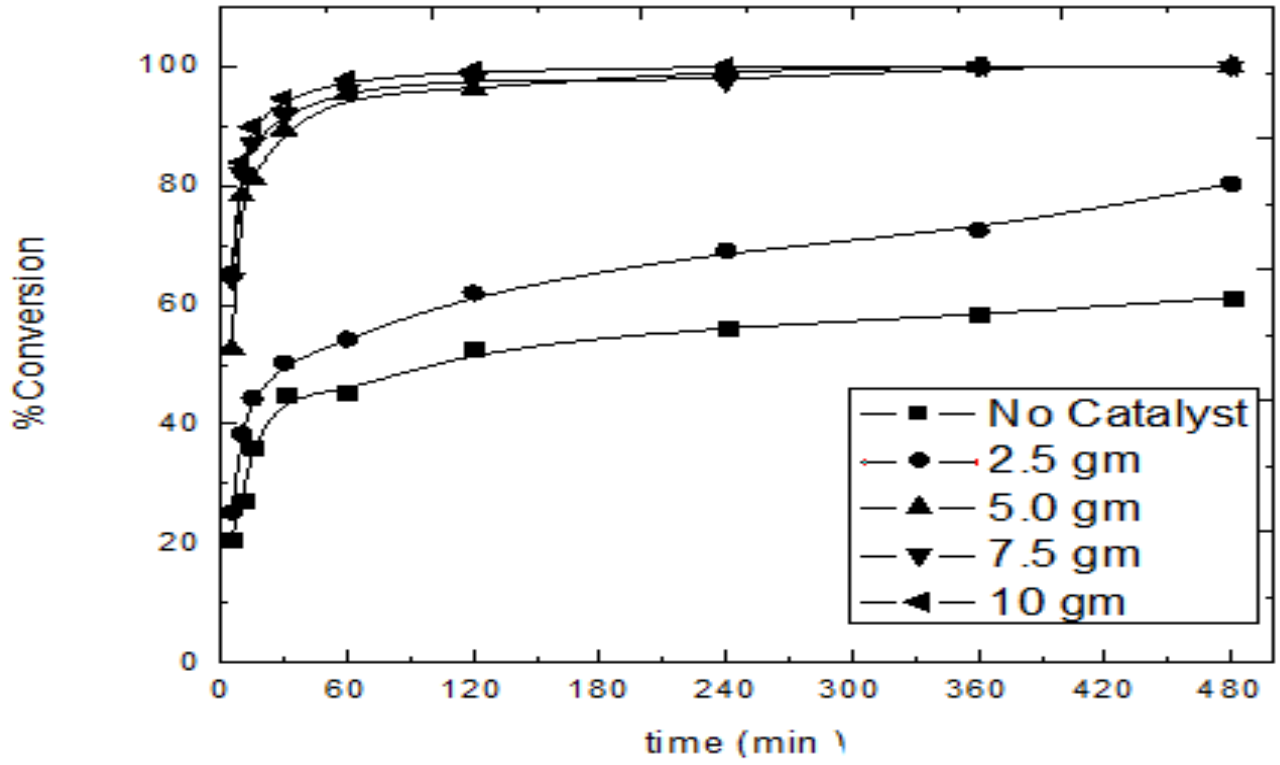


Figure 4.6: Effect of catalyst loading: Volume of Organic Phase = 50ml; Volume of BC = 15ml; Volume of Aqueous phase = 50ml; Sulfur loading= 3gm; Sulfide Concentration = 2.53kmol/m^3; MEA/H_2S mole ratio = 2.28; Stirring Speed =1500rpm; Temperature = 323 K.

To find out order of reaction, the initial reaction rate at different Amberlite IR400 concentration is calculated and its natural logarithm is plotted with natural logarithm of catalyst concentration as indicated in figure below.

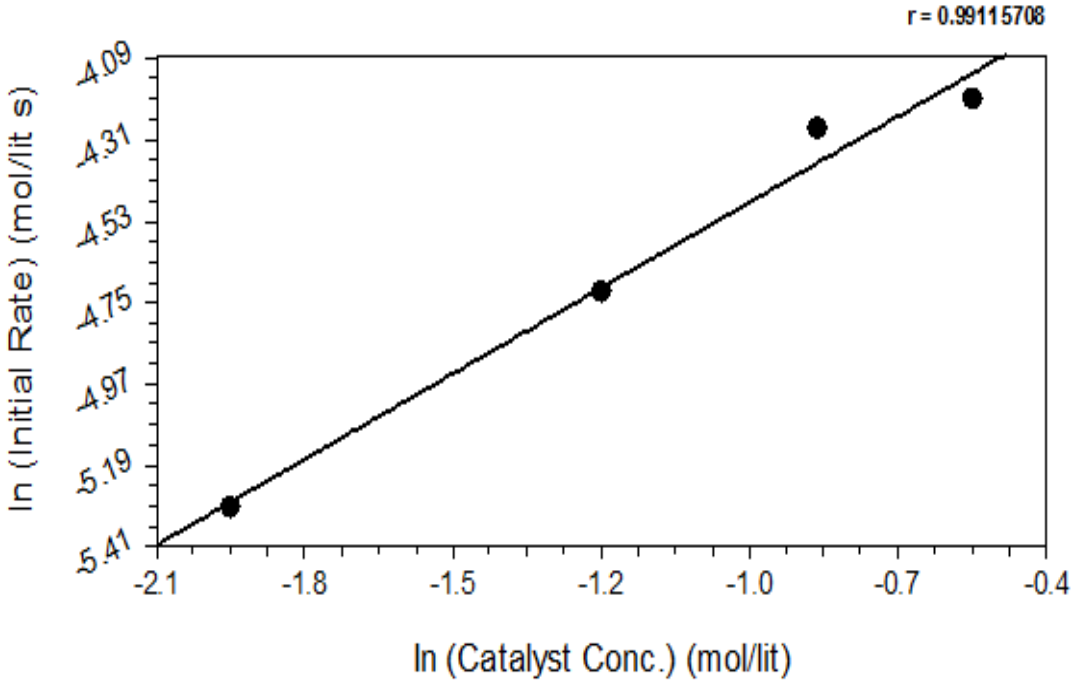


Figure 4.7: Plot of the natural logarithm of the initial rate vs the natural logarithm of the catalyst conc**.**

Volume of Organic Phase = 50ml; Volume of BC = 15ml; Volume of Aqueous Phase = 50ml; Sulfur loading= 3gm; Sulfide Concentration = 2.53kmol/m^3; MEA/H_2S mole ratio = 2.28; Stirring Speed =1500rpm, Temperature = 323 K

4.2.5 Effect of concentration of benzyl chloride

Since the reaction has been carried out with pure BC, the effect of initial concentration of BC on the conversion of BC was determined by changing the moles of BC at fixed sulfide concentration i.e., by varying initial BC/sulfide mole ratio. It is understood from this figure that with an increase in initial BC/sulfide mole ratio, BC conversion decreases because of the inadequate amount of sulfide in the aqueous phase. With initial BC/sulfide mole ratio of 0.70, 100%BC conversion was mentioned, whereas it was around 85% at low initial BC/sulfide mole ratio of 1.39 even after 480 min of reaction under otherwise identical experimental conditions as observed from the Fig. 4.8.To get maximum conversion with maximum selectivity of DBDS, lower range of initial BC/sulfide mole ratio is preferable.

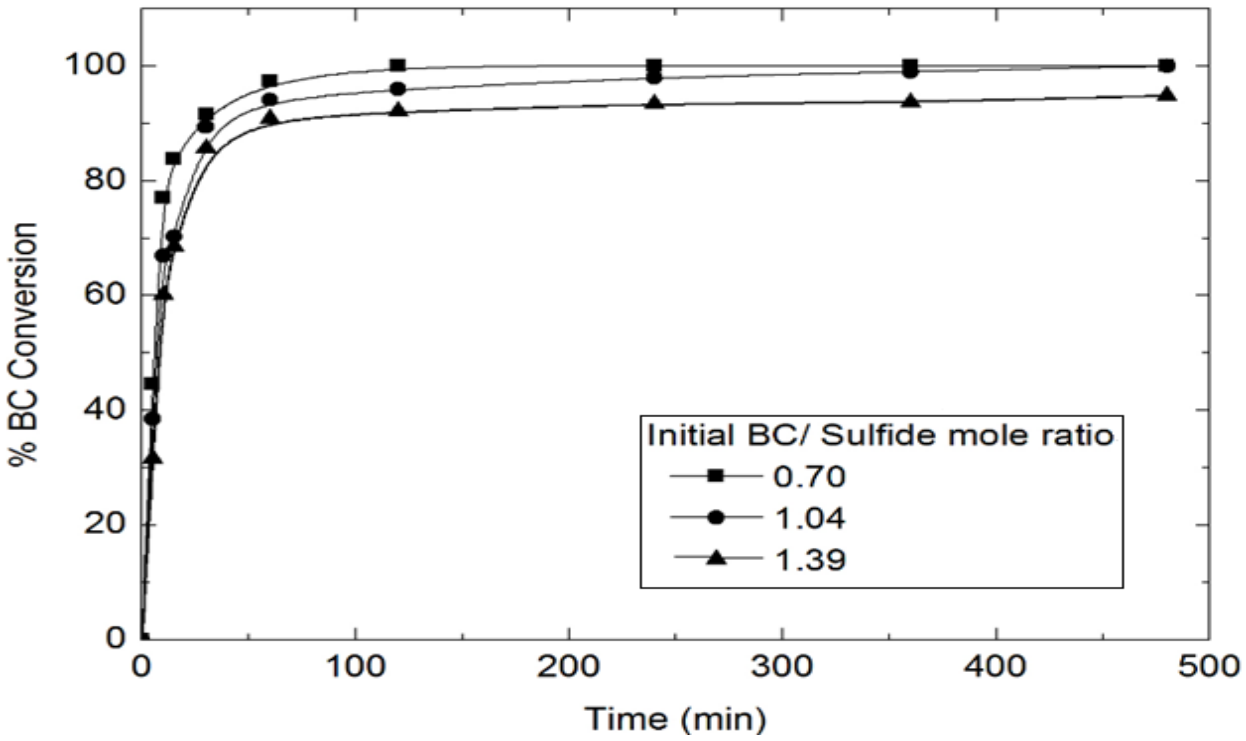


Figure 4.8: Effect of concentration of benzyl chloride: Volume of Organic Phase = 50ml; Volume of Aqueous Phase = 50ml; Sulfur loading=3gm; Catalyst loading= 5gm; Sulfide concentration = 2.53kmol/m^3; MEA/H_2S mole ratio = 2.28; Stirring Speed =1500rpm; Temperature = 323 K

4.2.6 Effect of sulfide concentration:

The effect of MEA to sulfide ratio was investigated by changing the amount of sulfide concentration in the aqueous phase at constant 35 weight% of the aqueous MEA solution. For fixed MEA concentration, with a reduction in initial sulfide concentration in the aqueous phase, the conversion of BC reduces as the initial concentration of sulfide in the aqueous phase as shown in Fig.4.9. At a fixed reaction condition, 100% conversion was reached after 480 min of run with the sulfide concentration of 2.5kmol/m^3.Continuous increase in sulfide concentration increases conversion as well as selectivity. Increased selectivity was observed due to increase in disulfide ions ($Q_2S_2^{2-}$) compare to sulfide ions.

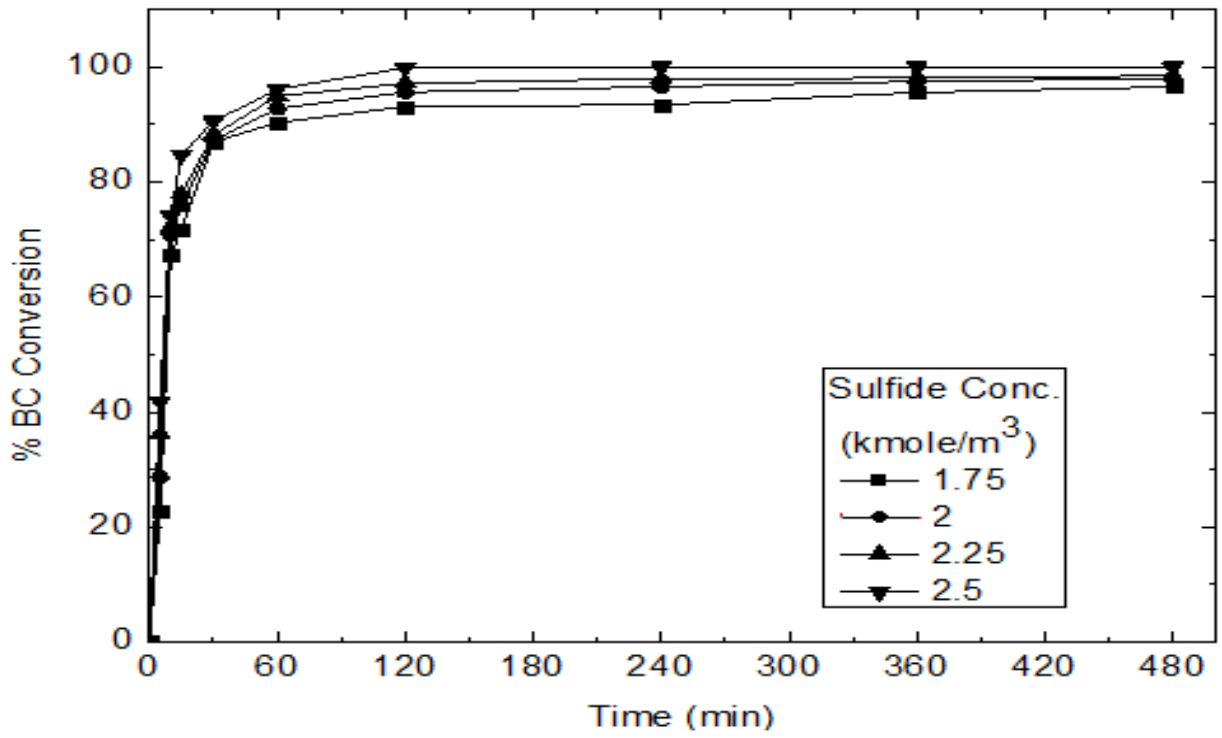


Figure 4.9: Effect of Sulphide Concentration: Volume of Organic Phase = 50ml; Volume of Aqueous Phase = 50ml; Sulfur loading=3gm; Catalyst loading= 5gm; MEA/H_2S mole ratio = 2.28; Stirring Speed =1500rpm, Volume of BC=15ml; Temperature = 323 K.

4.3 MECHANISTIC INVESTIGATION:

The mechanism of DBDS is explained in the description given below:

4.3.1 Mechanism of Triphase Catalysis

In the mechanism given by Stark, the PT catalyst travels easily between the organic and aqueous phases, yet in a TPC system, the catalyst movement is constrained and reagents of the aqueous and organic phase need to be transported to the catalyst cation accordingly. The catalyst active sites involved in the reaction are the one that are present on the interphase between the phases.

Most of the inorganic reactants or reagents are immiscible in the organic phase. Therefore, the reaction must be carried out at the aqueous-organic interface. Depending on the distribution of the product, the reaction mechanism was represented by the reactions of scheme 4.10. The product is obtained from the reaction contribution from both catalytic and non-catalytic pathway.

Non-catalytic Pathway: The dissolved sulfur and sulfide in aqueous phase forms an ion equilibrium to produce hydrosulfide, sulfide and disulfide ions shown in the figure below. These ion pairs react with aqueous MEA (RNH_2) to give aqueous reactants ammonium sulfide $(RNH_3)_2S$ and disulfide ($(NH_4)_2S_2$) via reaction (1)-(3). The aqueous reactant $(RNH_3)_2S$ and $(RNH_3)_2S_2$ react with organic reactant RX at the interface to yield a byproduct DBS and desired product DBDS respectively shown by reaction (7)-(9) in scheme below. The direct reaction of BC with $(RNH_3)_2S$ was assumed to proceed through an intermediate, $RSNH_3R$, which further reacts with RX to produce the byproduct DBS. Then $(RNH_3)_2S_2$ reacts with the reactant to form the product DBDS. The formed DBS and DBDS travels from interface to organic phase.

Catalytic Pathway: In the presence of catalyst, formed sulfide and disulfide ions from aqueous phase form catalyst active intermediate QSQ and Q_2S_2 respectively as shown in reaction 4-6. These active intermediate further reacts at interface with BC to give DBS and DBDS as shown by reaction 10-12. A Small quantity of sulfur in aqueous phase is responsible for HS- and S2- ion giving undesirable Benzyl mercaptan and DBS. Excess quantity of sulfur is responsible for synthesis of polysulfides. Therefore selectivity of product is increased by increasing the concentration of Q_2S_2 formed through maintaining sulfur concentration in aqueous. The formed product then travels from interface to organic phase shown in scheme below.

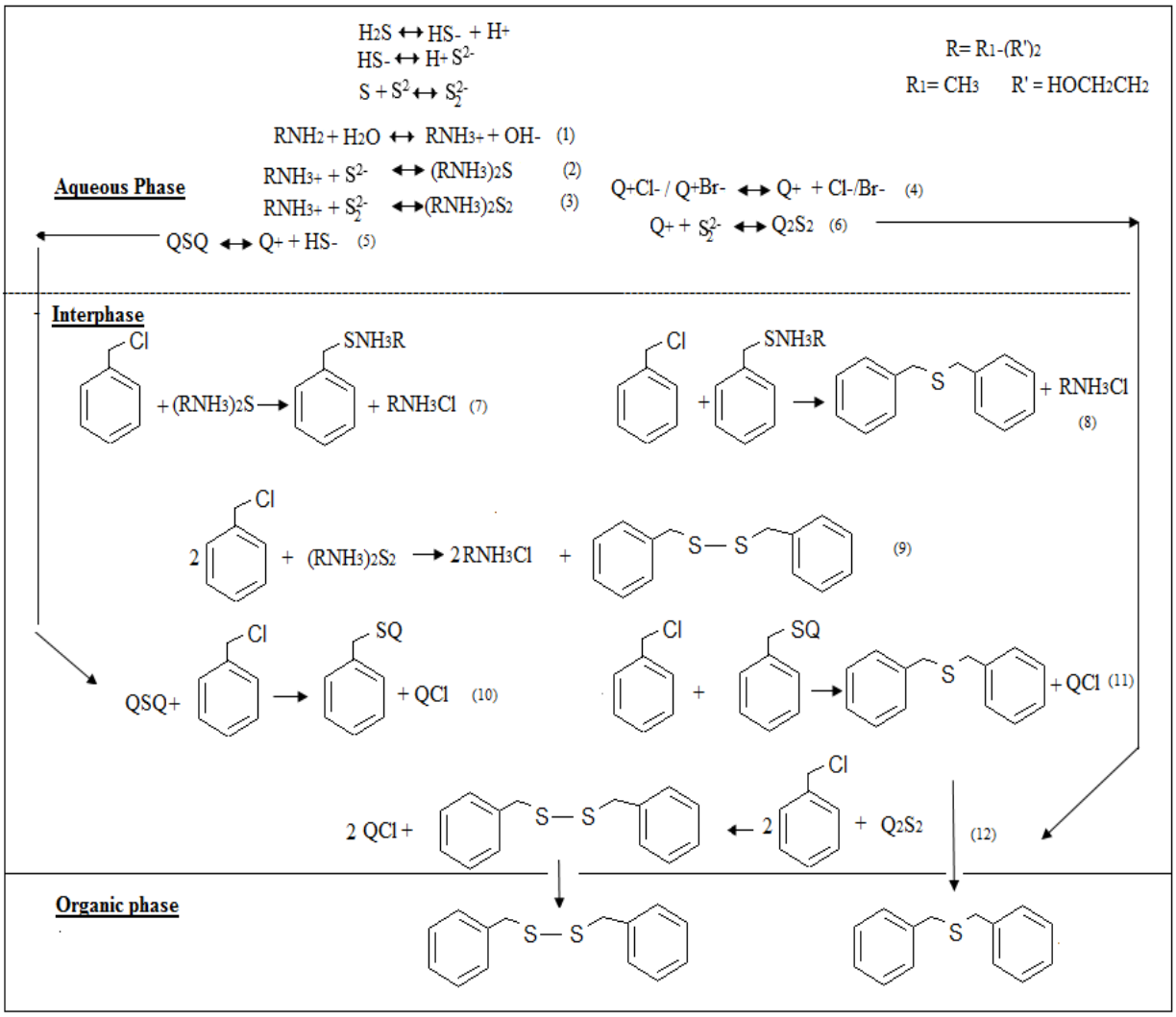


Figure 4.10 Mechanism Triphase Catalysis

4.4 RECYCLE AND REUSABILITY OF CATALYST (Amberlite IR 400)

After the completing the kinetic run, reaction mixture was charged into a separating funnel by pausing agitation and the phases was allowed to separate into three layers i.e. Liquid-Liquid Solid. When the aqueous and organic phases were completely separated, the catalyst was filtered from the solution by the use of filter paper. It was washed with acetone and water and was dried at around 50^0 C to remove the adsorbed substance. Then the dry catalyst was again reused for four times. The reusability of catalyst was observed better till three uses where a reduction in conversion was found during the fourth time since the quantity of third phase was very less as compared with the previous run as shown in Fig 4.11. Every time the catalyst was lost with aqueous

and organic phase during catalyst regeneration. The catalyst obtained was reused and the information obtained is shown in below figure.Fig.4.11 shows the conversion of benzyl chloride with the cycle number. It can be seen that after 3 cycles, the activity of tri phase catalyst Amberlite decreases. This tells that Amberlite has got excellent reuse property and high stability up to three use.

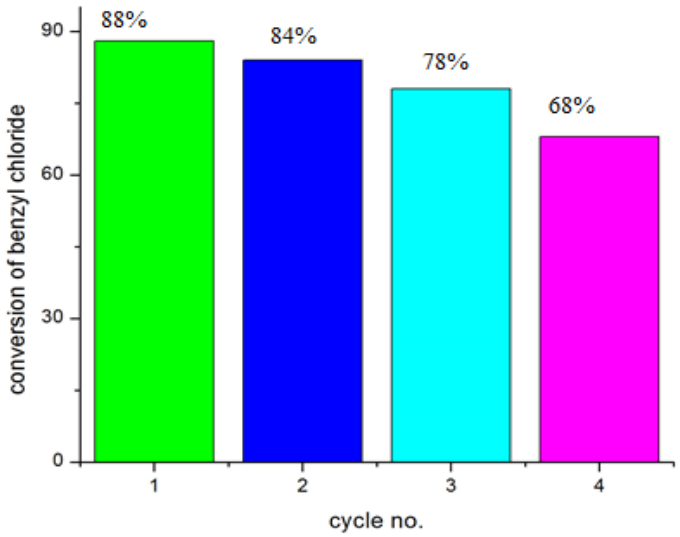


Figure 4.11 Conversion of Benzyl Chloride: Volume of Organic Phase = 50ml; Volume of Aqueous Phase = 50ml; Sulfide Concentration=2.53kmol/$m^{3,}$ Sulfur loading=3gm; Catalyst loading= 5gm; MEA/H_2S mole ratio = 2.28; Volume of BC= 15ml, Temperature = 323 K; Stirring speed =1500rpm

Chapter 5

SUMMARY AND CONCLUSIONS

Chapter 5

SUMMARY AND CONCLUSIONS

5.1 CONCLUSION:

The present work carried out in this thesis contributes to the evolution of a modernistic process to produce value-added chemicals utilizing the H_2S present in various byproduct gas streams. Since the removal of H_2S by alkanolamines being well established and industrially practiced by, the present work deals with a detailed written report of the production of value-added chemicals utilizingH_2S -rich aqueous alkanolamine in the batch mode.

The value-added chemicals produced in the present study are dibenzyldisulfide (DBDS), dibenzylsulfide and trisulfide from benzyl chloride (BC). The reaction of BC with H_2S-rich aqueous alkanolamines was conducted batch-wise in mien of an organic solvent under Liquid-Liquid-Solid mode with Amberlite IR 400 as PTC and sulfur powder. The impact of several process variables such as stirring speed, catalyst loading, elemental sulfur loading, sulfide concentration, reactant concentration and effect of temperature on the reaction rate, conversion, and selectivity was studied. A suitable mechanism was built utilizing the effects of different parameters on the rate of reaction and conversion to explain the course of the reaction. The two active ion pairs (Q_2S_2 and QSQ) formed in the aqueous phase are first moved to the organic phase where it reacts with BC to produce DBDS and DBS, respectively. Stirring speed has found to have almost no effect on conversion of benzyl chloride between 1000-2000 RPM, signifying no mass-transfer effect on reaction kinetics. The reaction rate was found to increase by changing temperature and catalyst concentration. The reaction is kinetically controlled having an apparent activation energy value of 22.4kJ/mol. Enhancement of production of dibenzyldisulfide was observed to increase in initial sulfide concentration. Increases in the concentration of BC decreases the conversion of BC and better selectivity of DBDS was achieved by adding adequate amount of sulfur. The catalytic activity of the catalyst, amberlite IR 400 was observed to decrease to 68% of the initial activity after 3 cycles. This reduction in catalytic activity is because of the loss of catalyst with aqueous and organic phase during regeneration. This tells that amberlite IR 400 has got high stability and exceptional reuse property up to three use.

In the reaction of BC with H_2S rich aqueous MEA, almost complete sulfide utilization in the aqueous phase was observed under certain experimental conditions. Therefore it needs no further treatment before its reuse for the removal of H_2S. Therefore, present process has enormous potential to be considered as a feasible option to conventional process.

5.2 FUTURE WORK

.

5.2.1 Finding out Effect of other Parameters

Effect of other anions as co-catalyst and the effect of the MEA concentration on addition of weak base like NaOH that can act upon the response rate and selectivity of the desired product can also be tested. In the present study, toluene has been utilized as a solvent in most of the cases because it is inexpensive. The physical of organic solvent play an important part of the PTC reaction, not only by acting upon the intrinsic organic reaction but also by affecting the transport properties of PTC and active catalyst species (QSQ and QSH) (Yang et al., 2003). Other types of solvents like chlorobenzene, n-heptane, and dichloromethane can be tried out. Other aqueous solution can be utilized such as DEA and MDEA based on the different type of gas stream. Absorption using MDEA will be best suited for selective removal of H_2S, if the gas stream contains CO_2 with H_2S. Tri sulfides and poly sulfides can also be prepared selectively by adjusting the amount of sulfur in the aqueous phase.

References

1. Dehmlow, E. V.; Dehmlow, S. S. Phase transfer catalysis, 2nd ed., Verlag Chemie Weinheim.1983.
2. Hamblin, R. Removal and recovery of sulfur from a gas stream containing hydrogen sulfide. Patent No. US3728441, 1973.
3. Harvey, W. W.; Makrides, A.C. Process for Removing Hydrogen Sulfide and Ammonia from Gaseous Streams. Patent No. US4192854, 1980.
4. Maity, S.K.; Pradhan, N.C; Patwardhan, A. V. Reaction of benzyl chloride with ammonium sulfide under liquid–liquid phase transfer catalysis: Reaction mechanism and kinetics. Appl. Catal. A: Gen. 2006a, 250, 114–121.
5. Maity, S.K.; Pradhan, N.C; Patwardhan, A. V. Kinetics of the reduction of nitrotoluenes by aqueous ammonium sulfide under liquid–liquid phase transfer catalysis .Appl. Catal. A: Gen. 2006b, 301, 251–258.
6. Maity, S.K.; Pradhan N.C; Patwardhan, A.V. Kinetics of reduction of nitrotoluenes byH_2S rich aqueous ethanolamine. Ind. Eng. Chem. Res. 2006c, 45, 7767-7774.
7. Maity, S.K.; Pradhan N.C; Patwardhan, A.V. Reduction of o-nitroanisole to o-anisidinebyH$_2$S-richaqueousdiethanolamine: A novel process for utilization ofH_2S-ladengas streams, Chem. Eng. Sc. 2007, 62, 805-813.
8. Melville, J. B.; Goddard, J. D. Solid-liquid phase-transfer catalysis in rotating-disk flow. Industrial &. Engineering Chemistry Research 1988, 27, 551-555.
9. Naik, S. D.; Doraiswamy, L. K. Mathematical modelling of solid-liquid phase transfer catalysis. Chemical Engineering Science 1997, 52(24), 4533-4546.
10. Pradhan, N. C.; Sharma, M. M. Kinetics of reactions of benzyl chloride/p-Chlorobenzyl chloride with sodium sulfide: phase-transfer catalysis and the role ofthe omega phase. Industrial & Engineering Chemistry Research 1990, 29, 1103-1108.
11. Pradhan, N. C.; Sharma, M. M. Solid-liquid reactions catalyzed by alumina and ion exchange resin: Reactions of benzyl chloride/ p-chlorobenzyl chloride with solid sodium sulfide. Industrial & Engineering Chemistry Research 1992a, 31, 1610-1614.
12. Starks, C. M. Phase transfer catalysis. I. Heterogeneous reactions involving anion transfer by quaternary ammonium and phosphonium salts. Journal of the American Chemical Society1971, 93, 195-199.

13. Starks, C. M.; Liotta, C. L. Phase-transfer catalysis principles and techniques. Academic, New York, 1978.
14. Starks, C.M., Liotta, C.L., Halpern, M. Phase transfer catalysis. Chapman & Hall, New York, USA, 1994.
15. Yadav, G. D.; Lande, S. V. Liquid-liquid-liquid phase transfer catalysis: a novel and green concept for selective reduction of substituted nitroaromatics. Advanced Synthesis & Catalysis 2005, 347, 1235-1241.
16. Yadav, G. D.; Lande, S. V. Intensification of rates and selectivity using tri-liquid versus biliquid phase transfer catalysis: insight into reduction of 4-nitro-oxylenewithsodium sulfide. Industrial & Engineering Chemistry Research 2007, 46, 2951-2961.
17. Yadav, G. D.; Naik, S. S. Novelties of liquid-liquid-liquid phase transfer catalysis: alkoxylation of p-chloronitrobenzene. Catalysis Today 2001, 66, 345-354.
18. Yadav, G.D., Jadhav, Y.B., 2003a. Kinetics and modelling of liquid–liquid phase transfer catalysed synthesis of p-chlorophenyl acetonitrile: role of co-catalyst in intensification of rates and selectivity. Journal of Molecular Catalysis A: Chemical 2003a, 192, 41–52.
19. Yadav, G. D.; Jadhav, Y. B.; Sengupta, S. Novelties of kinetics and mechanism ofliquid–liquid phase transfer catalyzed reduction of p-nitroanisole to p-anisidine.Chemical Engineering Science 2003b, 58, 2681 - 2689.
20. Yadav, G. D.; Jadhav, Y. B.; Sengupta, S. Selectivity engineered phase transfer catalysis in the synthesis of fine chemicals: reactions of p-chloronitrobenzene with sodium sulphide. Journal of Molecular Catalysis A: Chemical 2003c, 200,117-129.
21. Yadav, G. D.; Reddy, C. A. Kinetics of the n-butoxilation of p-chloronitrobenzene under liquid-liquid-liquid phase transfer catalysis. Industrial &Engineering Chemistry Research 1999, 38 (6), 2245-2253.
22. Yadav, G. D.; Sharma, M. M. Kinetics of reactions of benzyl chloride with sodium acetate/benzoate: phase transfer catalysis in solid-liquid system. Industrial &Engineering Chemistry Process Design and Development 1981, 20, 385-390.
23. Yang, H.M., Lin, C.L. Phase-transfer catalysed benzylation of sodium benzoate usingaliquat-336 as catalyst in liquid–liquid system. Journal of Molecular Catalysis A: Chemical2003, 206, 67–76.

24. Polshettiwar, V.; Nivsarkar, M.; Acharya, J.; Kaushik, M.P. A new reagent for the efficient synthesis of disulfides from alkyl halides. Tetrahedron Letters2003, 44, 887-889.
25. Thurow, S.; Pereira, V.A.; Martinez, D.M.; Alves, D.; Perin, G.; Jacob R.G.;Lenardão, E.J. Base-free oxidation of thiols to disulfides using selenium ionic liquid. Tetrahedron Letters2011, 52, 640-643.
26. Sonavane, S.U.; Chidambaram, M.; Khalil, S.; Almog, J.; Sasson, Y. Synthesis of cyclic disulfides using didecyldimethylammonium bromide as phase transfer catalyst. Tetrahedron Letters2008, 49, 520-522.
27. Sonavane, S.; Chidambaram, M.; Almog, J.; Sasson, Y. Rapid and efficient synthesis of symmetrical alkyl disulfides under phase transfer conditions. Tetrahedron Letters2007, 48, 6048-6050.
28. Bandgar, B.P.; Uppalla, L.S.; Sadavarte, V.S. Reduction of sulfur with borohydride exchange resin in methanol: application to rapid and selective synthesis of disulfides. Tetrahedron Letters2001, 42, 6741-6743.
29. Ruggles, E.L.; Hondal, R.J. Synthesis and properties of disulfide-bond containing eight-membered rings. Tetrahedron Letters200647, 4281-4284.